THE SECOND VIRIAL COEFFICIENTS OF SOME GAS MIXTURES

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Summary

The second virial coefficients of the mixtures CH_4—$C(CH_3)_4$, CH_4—$Si(CH_3)_4$, and CH_4—SF_6 have been measured for several compositions and at several temperatures.

Values of the coefficients B_{12}, derived from the results, fail to conform to Guggenheim and McGlashan's (1951) extension of the principle of corresponding states. Reasons are given for this disagreement.

I. Introduction

The second virial coefficient B_m of a mixture of two gases 1 and 2 is related to their mole fractions x_1 and x_2, and their virial coefficients B_{11} and B_{22}, by the expression

$$B_m = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}, \quad \ldots\ldots\ldots\ldots \quad (1)$$

where B_{12} is a quantity characteristic of the interaction of two isolated molecules 1 and 2; it varies with the temperature but not with the composition of the mixture.

Guggenheim and McGlashan (1951) showed that B_{12} may be derived from the properties of the components 1 and 2 by the principle of corresponding states and by assuming that the interaction energy of the pair of unlike molecules 1—2 bears a particular relation to the interaction energies of the pairs 1—1 and 2—2. This treatment is most successful when the components of the mixtures obey the principle of corresponding states. It gives good results for mixtures of simple non-polar gases (Guggenheim and McGlashan 1951), but it fails when both components are polar (Fox and Lambert 1951). In the present work we have tested the validity of the method for mixtures of two types of molecules, both of which are non-polar and nearly spherical, but which differ considerably in size and complexity.

We shall describe measurements of B_{12} for the mixtures:

Methane-*neo*pentane,
Methane-tetramethylsilane,
Methane-sulphur hexafluoride,

and show that the results do not conform to Guggenheim and McGlashan's

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treatment. The cause of the disagreement appears to lie both in the inapplicability of the principle of corresponding states to these mixtures and in the failure of the assumed averaging rules for the intermolecular energies.

II. Experimental

(*a*) *Apparatus and Method*

The compressibility apparatus has been described before (Hamann and Pearse 1952 ; Hamann, McManamey, and Pearse 1953) and it is only necessary to discuss the methods of preparing and analysing the gas mixtures.

(i) *Synthesis.*—The gases were mixed in the compressibility apparatus itself. The first gas, methane, was introduced into the left-hand burette where it was confined over mercury and its pressure was measured in an accurately known volume. The second gas was then added by gradually increasing its pressure in the inlet tube until it bubbled through the mercury into the lowest bulb of the same burette. To ensure efficient mixing the mercury was raised until the whole of the gas was enclosed in the top bulb and it was left there for about 20 hours. The composition of the mixture was calculated from the total pressure and the initial pressure of methane, small corrections being applied for the imperfection of the gases. Later mixtures were prepared by removing some of the gas from the burette, measuring the amount remaining, and adding more of the second component.

(ii) *Analysis.*—Each composition was checked by analysing the gas removed from the burette. It was introduced into a small glass bulb where its pressure was measured, then it was frozen in liquid nitrogen, and the methane (vapour pressure : 10 mm Hg at −195 °C) was pumped off to leave the second component. This was warmed and its pressure measured in the same total volume as before. The process of freezing, pumping, and warming was repeated until the residual pressure no longer decreased. The total and partial pressures, with virial corrections, gave another value for the mole fraction of the second component. This was always within 1 per cent. of the value from the synthesis, and served, not only to confirm that estimate, but also to show that the gases had been well mixed. The mean of the two figures was used in calculating B_{12}.

(*b*) *Materials*

(i) *Methane* was prepared by hydrolysing methyl magnesium bromide. It was passed through water and then sulphuric acid into a trap immersed in liquid nitrogen boiling under reduced pressure. Volatile impurities were pumped off, the liquid nitrogen was removed, and the middle fraction of gas was collected as the solid slowly warmed.

(ii) neo*Pentane* was formed by the reaction of *tert.*-butyl magnesium iodide with dimethyl sulphate in ether. It was bubbled through sulphuric acid and fractionally distilled. The vapour pressure at 0 °C was 534 mm Hg, compared with 532 mm Hg (from *Selected Values of the Properties of Hydrocarbons*).

(iii) *Tetramethylsilane* was prepared by the method of Bygdén (1914). Silicon tetrachloride was added to an ethereal solution of methyl magnesium

bromide and the product was refluxed with sodium ethoxide to remove methyl bromide, and with sulphuric acid to remove ether. It was distilled and the fraction boiling between 26 and 27 °C was collected and sublimed at a low temperature in a vacuum system to remove dissolved air.

(iv) *Sulphur Hexafluoride.*—The commercial product was purified as described earlier (Hamann, McManamey, and Pearse 1953).

III. Results

The measurements of each isotherm gave four values for the quantity $B'=V(PV/RT-1)$, corresponding roughly to the pressures $\frac{1}{2}$, 1, $1\frac{1}{2}$, and 2 atm. We found that when $-B'$ was less than 400 cm^3 g-mol^{-1} it was independent of the pressure and therefore represented the true second virial coefficient $-B$. Some of the larger values of $-B'$ changed slightly with the pressure, presumably because of the influence of the third and higher virial coefficients. $-B$ was then taken to be the limit of $-B'$ at zero pressure.

Our apparatus was not suited to the precise measurement of the small second virial coefficient of pure methane, and since the derived values of B_{12} are sensitive to this coefficient, we have used the best values obtainable from the data of Keyes and Burks (1927), Michels and Nederbragt (1936), and Olds *et al.* (1943). A comparison of these with some of our own measurements is given below:

	$-B$/cm^3 g-mol^{-1} for Methane					
T (°K)	303·16	323·16	333·16	343·16	363·16	383·16
Present work ..	38·2	35·2	33·9	28·5	22·7	19·7
Earlier sources —	41·6	34·6	31·8	29·1	24·2	19·5

The results for the three binary systems are listed in Tables 1–3.

TABLE 1

SECOND VIRIAL COEFFICIENTS OF METHANE-NEOPENTANE MIXTURES

The coefficients are in the units cm^3 g-mol^{-1}

T (°K)	$-B_m$						$-B_{12}$				Mean $-B_{12}$
	Mole Fraction of *neo*Pentane						Mole Fraction of *neo*Pentane				
	0	0·180	0·357	0·608	0·696	1·000	0·180	0·357	0·608	0·696	
303·16	41·6	109	197	401	473	842	182	158	175	145	165
323·16	34·6	90	170	344	414	734	145	135	141	131	138
333·16	31·8	84	161	325	385	686	137	132	140	118	132
343·16	29·1	76	149	299	361	643	121	120	119	111	118
353·16	26·6	72	139	283	338	602	117	112	118	104	113
363·16	24·2	67	130	265	319	566	110	104	109	101	106
383·16	19·5	59	114	236	284	507	100	90	96	86	93
403·16	15·4	48	102	208	249	452	78	83	81	68	78

There are sometimes large differences between the values of B_{12} for a particular temperature and different compositions. They are no greater than we should expect from the likely errors in the virial coefficients and compositions

TABLE 2

SECOND VIRIAL COEFFICIENTS OF METHANE-TETRAMETHYLSILANE MIXTURES

The coefficients are in the units $cm^3\ g\text{-}mol^{-1}$

T (°K)	$-B_m$ Mole Fraction of Tetramethylsilane						$-B_{12}$ Mole Fraction of Tetramethylsilane				Mean $-B_{12}$
	0	0·246	0·334	0·568	0·799	1·000	0·246	0·334	0·568	0·799	
323·16	34·6	131	187	389	656	956	144	146	151	138	145
333·16	31·8	121	173	358	610	886	133	135	135	134	134
343·16	29·1	114	162	336	568	831	127	127	127	113	124
353·16	26·6	107	151	310	534	784	120	116	106	101	111
363·16	24·2	99	141	292	506	737	110	108	101	107	106
383·16	19·5	87	122	258	449	649	99	92	92	106	97
403·16	15·4	76	108	229	402	580	87	82	79	97	86

TABLE 3

SECOND VIRIAL COEFFICIENTS OF METHANE-SULPHUR HEXAFLUORIDE MIXTURES

The coefficients are in the units $cm^3\ g\text{-}mol^{-1}$

T (°K)	$-B_m$ Mole Fraction of Sulphur Hexafluoride				$-B_{12}$ Mole Fraction of Sulphur Hexafluoride		Mean $-B_{12}$
	0	0·318	0·639	1·000	0·318	0·639	
313·16	37·9	80	148	253	85	86	85
333·16	31·8	67	126	223	68	67	68
353·16	26·6	56	108	192	56	57	57
373·16	21·8	45	91	163	42	47	45
393·16	17·4	39	75	145	37	29	33

of the mixtures. It is worth noting that there are comparably large differences to be found in many of the recorded measurements on gaseous mixtures. For example, Beattie and Stockmayer's (1942) second virial coefficients for mixtures of methane and *n*-butane yield values of B_{12}, which vary by as much as 23 $cm^3\ g\text{-}mol^{-1}$ for different compositions.

IV. DISCUSSION

Pitzer (1939) showed that if a gas is to conform to the principle of corresponding states it is necessary that the interaction energy ε between its molecules be of the form :

$$\frac{\varepsilon}{\varepsilon^*} = f\left(\frac{r}{r^*}\right), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where r is the distance between the molecules, ε^* is an energy and r^* is a length, both characteristic of the interacting molecules, and f is a universal function. Subsequently Guggenheim and McGlashan (1951) demonstrated that the condition (2), applied to binary mixtures, leads to the results:

$$\frac{B_{11}}{V_{11}^*}=\varphi\left(\frac{T}{T_{11}^*}\right), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$\frac{B_{22}}{V_{22}^*}=\varphi\left(\frac{T}{T_{22}^*}\right), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$\frac{B_{12}}{V_{12}^*}=\varphi\left(\frac{T}{T_{12}^*}\right), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where φ is another universal function, T is the absolute temperature, and $T_{11}^*, \ldots V_{11}^*, \ldots$, are characteristic temperatures and volumes satisfying the relations:

$$\frac{T_{11}^*}{\varepsilon_{11}^*}=\frac{T_{22}^*}{\varepsilon_{22}^*}=\frac{T_{12}^*}{\varepsilon_{12}^*}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$\frac{V_{11}^*}{(r_{11}^*)^3}=\frac{V_{22}^*}{(r_{22}^*)^3}=\frac{V_{12}^*}{(r_{12}^*)^3}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

T_{11}^*, T_{22}^* and V_{11}^*, V_{22}^* may conveniently be taken as the critical temperatures T_c and critical volumes V_c of the pure gases, but it is more difficult to see what values should be assigned to T_{12}^* and V_{12}^*. Guggenheim and McGlashan used the plausible averaging rules

$$\varepsilon_{12}^*=(\varepsilon_{11}^*\varepsilon_{22}^*)^{\frac{1}{2}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$r_{12}^*=\tfrac{1}{2}(r_{11}^*+r_{22}^*), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

to derive the relations:

$$T_{12}^*=(T_{11}^*T_{22}^*)^{\frac{1}{2}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$(V_{12}^*)^{\frac{1}{3}}=\tfrac{1}{2}(V_{11}^*)^{\frac{1}{3}}+\tfrac{1}{2}(V_{22}^*)^{\frac{1}{3}}, \quad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

and showed that these were successful for a variety of mixtures.

TABLE 4

CRITICAL CONSTANTS OF THE PURE GASES

Gas	T_c (°K)	V_c (cm³ g-mol⁻¹)
CH_4	191·1*	99·0*
$C(CH_3)_4$.. ..	433·8*	303*
$Si(CH_3)_4$ ..	460±20†	380±35†
SF_6	318·7*	194*

* From the review by Kobe and Lynn (1953).

† Estimated from a number of empirical formulae listed by Partington (1949) and based on the freezing and boiling temperatures and the density of liquid $Si(CH_3)_4$.

We have applied this method to our experimental results, using the critical constants listed in Tables 4 and 5.

The reduced second virial coefficients B/V^* of the pure and mixed gases are plotted against reduced temperatures T/T^* in Figures 1 and 2. It will be seen that, although the points for the pure gases lie close to the general plot of gases obeying the principle of corresponding states, those for the mixtures

TABLE 5

PSEUDO-CRITICAL CONSTANTS OF MIXTURES

Calculated from equations (**10**) and (**11**)

Mixture	T^*_{12} (°K)	V^*_{12} (cm³ g-mol⁻¹)
CH_4—$C(CH_3)_4$ ..	288	182
CH_4—$Si(CH_3)_4$ ..	296	209
CH_4—SF_6	247	141

diverge markedly. The cause of this deviation could lie in the failure, either of the averaging rules (**10**) and (**11**), or of the condition (**2**).

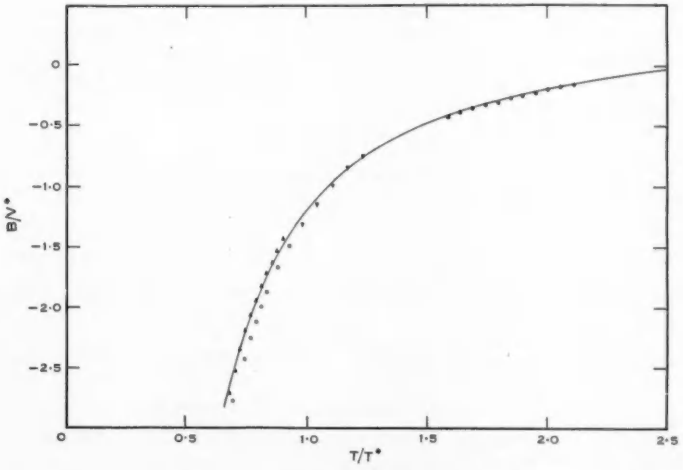

Fig. 1.—Experimental reduced second virial coefficients for pure gases. The curve is defined by equation (**17**) of a review by Guggenheim (1953).
● Methane. ○ *neo*Pentane. ▲ Tetramethylsilane. ▼ Sulphur hexafluoride.

We may examine this problem in terms of a theory recently developed (Hamann and Lambert 1954) to explain the properties of pure fluids of complex but nearly spherical molecules. In this theory the interaction energy between two complex molecules was assumed to be the sum of all the interactions between point centres of force at the positions of each atom, averaged for all orientations of the molecules. The method is readily extended to mixtures. As an example

we shall consider the interaction of a monatomic gas A with one composed of hypothetical tetrahedral molecules AA_4. To the approximation that the weak forces between hydrogen atoms can be ignored, this is a realistic model for mixtures of methane and *neo*pentane and it should apply qualitatively to the other two mixtures.

Denoting the spherically smoothed interaction potential between a single atom and a shell of four atoms by v, that between two shells of four atoms each by w, and that between two single atoms by u, we have the total interaction energies :

Interaction :	$A-A$	$A-AA_4$	AA_4-AA_4
Potential energy :	$\varepsilon_{11}=u$	$\varepsilon_{12}=u+v$	$\varepsilon_{22}=u+2v+w$,

where the terms v and w depend upon the form of u and on the bond length in the AA_4 molecule. Taking u to be a Lennard-Jones (12,6) potential and selecting

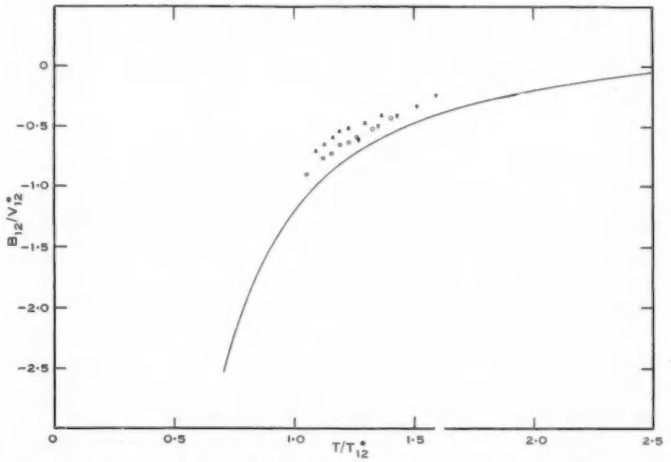

Fig. 2.—Experimental values of B_{12}/V_{12}^* for three mixtures. The curve is the same as that in Figure 1.

○ Methane-*neo*pentane. ▲ Methane-tetramethylsilane. ▼ Methane-sulphur hexafluoride.

a representative bond length we have previously (Hamann and Lambert 1954, equation (**12**)) carried out the integrations for v and w. We can use these results to derive the relations between the minimum interaction energies and equilibrium separations for the three types of molecular encounter. They are listed in Table 6. The relations (**8**) and (**9**) give the values in parentheses in Table 6. Although the method of averaging r^* is good, the geometric mean of ε_{11}^* and ε_{22}^* is in error by 6 per cent. in a direction to cause apparent deviations of the type seen in Figure 2.

Of course, Figure 2 is drawn in units of T_{12}^* and V_{12}^*, not of ε_{12}^* and $(r_{12}^*)^3$ and we must consider the reliability of the additional relations (**6**) and (**7**).

This can be done most easily if the characteristic parameters T^* and V^* are taken, not as the critical temperature and volume, but as the Boyle temperature

TABLE 6
THEORETICAL MOLECULAR INTERACTION PARAMETERS

Interaction	Minimum Potential Energy	Intermolecular Distance at Minimum Potential
$A—A$	$-\varepsilon_{11}^*$	r_{11}^*
$A—AA_4$	$-\varepsilon_{12}^*=-1\cdot53\varepsilon_{11}^*$ $(-1\cdot62\varepsilon_{11}^*)$	$r_{12}^*=1\cdot375r_{11}^*$ $(1\cdot37r_{11}^*)$
$AA_4—AA_4$	$-\varepsilon_{22}^*=-2\cdot64\varepsilon_{11}^*$	$r_{22}^*=1\cdot74r_{11}^*$

T_B at which the second virial coefficient changes sign and the Boyle volume V_B defined by

$$V_B=T_B\left(\frac{\mathrm{d}B}{\mathrm{d}T}\right)_{T=T_B}.$$

We have previously listed T_B and V_B for the (12,6) potential $\varepsilon_{11}=u$ and we have now derived these quantities for the other two potentials, $\varepsilon_{12}=u+v$ and $\varepsilon_{22}=u+2v+w$, by numerically integrating the formula

$$B=-2\pi N\int_0^\infty (\mathrm{e}^{-\varepsilon/kT}-1)r^2\mathrm{d}r,$$

where N is Avogadro's number and k is Boltzmann's constant. The results are given in Table 7. Clearly the conditions (6) and (7) are not satisfied.

TABLE 7
THEORETICAL BOYLE CONSTANTS

Interaction	kT_B	V_B/N
$A—A$	$3\cdot41\varepsilon_{11}^*$	$1\cdot19\,(r_{11}^*)^3$
$A—AA_4$ ..	$2\cdot22\varepsilon_{12}^*$	$1\cdot53\,(r_{12}^*)^3$
$AA_4—AA_4$ ..	$1\cdot73\varepsilon_{22}^*$	$1\cdot76\,(r_{22}^*)^3$

If we combine the information given in Tables 6 and 7 we can then write the different Boyle constants in the same units (Table 8). We are now in a position to assess the total error due to the failure of the conditions (6) to (9).

TABLE 8
THEORETICAL BOYLE CONSTANTS

Interaction	kT_B/ε_{11}^*	$V_B/N(r_{11}^*)^3$
$A—A$	$3\cdot41$	$1\cdot19$
$A—AA_4$	$3\cdot40$	$3\cdot97$
	$(3\cdot95)$	$(3\cdot95)$
$AA_4—AA_4$	$4\cdot57$	$9\cdot27$

The rules (10), (11) yield the average values shown in parentheses in Table 8; they give the correct pseudo-Boyle volume $(V_B)_{12}$ but overestimate the pseudo-Boyle temperature $(T_B)_{12}$ by 16 per cent. Figure 3 shows that this displaces

the plot of $B_{12}/(V_B)_{12}$ in the same direction, and by roughly the same amount, as the experimental points deviate from the curve for well-behaved gases in Figure 2.

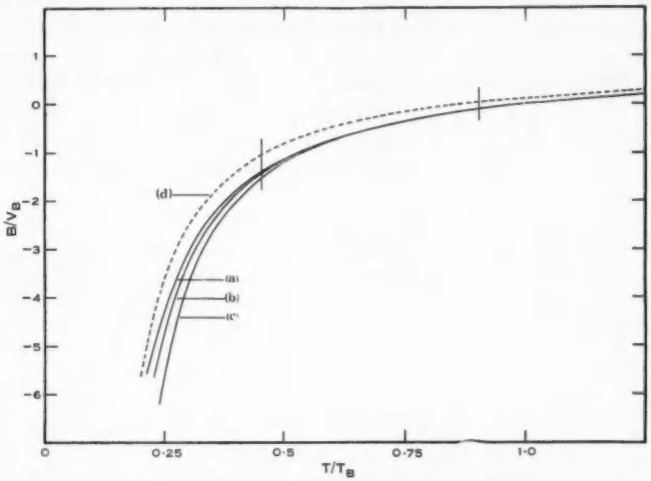

Fig. 3.—Theoretical second virial coefficients reduced by the Boyle parameters. Curves (*a*) and (*c*) are for the pure gases *A* and AA_4 respectively; curve (*b*) is a plot of $B_{12}/(V_B)_{12}$ against $T/(T_B)_{12}$, using the correct values of $(V_B)_{12}$ and $(T_B)_{12}$ from Table 8; curve (*d*) is a similar plot based upon the incorrect values of $(V_B)_{12}$ and $(T_B)_{12}$ averaged by equations (**10**) and (**11**). (The vertical lines indicate the range of the experimental points plotted in Fig. 2.)

It appears that these mixtures fail to conform to Guggenheim and McGlashan's treatment, (i) because they do not satisfy the condition for corresponding states (equation (**2**)), and (ii) because of the inaccuracy of the geometric mean rule for interaction energies.

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POLAROGRAPHY OF SOME COORDINATION COMPOUNDS OF PLATINUM

I. HEXAMMINEPLATINUM(IV) AND TRIS(ETHYLENEDIAMINE)PLATINUM(IV) IONS

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Summary

The polarographic reduction of tris(ethylenediamine)platinum(IV) and the hexammineplatinum(IV) ions has been studied in potassium chloride, potassium nitrate, and potassium nitrate plus ammonia solutions. Both ions were reduced irreversibly producing similarly shaped waves, showing well-defined diffusion current regions corresponding to two-electron reductions of the complexes. A linear relationship existed between diffusion current and concentration within the range examined. In aqueous potassium chloride and potassium nitrate media, the waves contained slight inflexions at positions corresponding to one-electron additions. The phenomenon suggested the transient presence of platinum(III) ions, and indicated that the half-wave potential of the reduction of the complexes to the trivalent state was very close to the half-wave potential of the reduction from platinum(IV) to platinum(II). The values were so close together as to indicate the improbability of isolating the trivalent complexes. Gelatin enhanced the inflexion in the wave but shifted the wave in a more negative direction. An increased concentration of supporting electrolyte also shifted the wave to a more negative position. In all cases a continuous discharge began at about —1·3 V (*v.* S.C.E.). This discharge was so far removed from that of the potassium ions of the supporting electrolyte that it was attributed to the discharge of hydrogen. Since the initial reduction of the platinum complexes corresponded to a two-electron change, it can be represented by reduction to a tetrammine ion. It is postulated that at higher applied potentials (namely, —1·3 V *v.* S.C.E.) the reduction proceeded further, producing platinum metal. This platinum metal would be in an active state, insoluble in mercury, and being on the surface, would lower the overvoltage of hydrogen leading to its discharge at a more positive potential than on a pure mercury surface. This view was supported by the fact that gas bubbles were observed at the dropping electrode when a voltage greater than —1·3 V was applied to the electrode for some time. When ammonia was added to the supporting electrolyte, a wave, without an inflexion, and corresponding to an irreversible two-electron reduction, was obtained at more negative potentials. The bivalent tetrammineplatinum(II) and bis(ethylenediamine)platinum(II) ions also gave polarograms showing the continuous discharge of hydrogen.

I. INTRODUCTION

Very little work has been published on the behaviour of compounds of platinum at the dropping mercury electrode (D.M.E.). Willis (1945) studied the behaviour of potassium tetrachloroplatinate(II) in various complexing media. No reduction waves were obtained. English (1950) studied the reduction of the hexachloroplatinate(IV) ion as a means of estimating platinum in organic materials. Laitinen and Onstott (1950) have studied the reduction of the tetrachloroplatinate(II) ion.

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Whereas much work has been published on the polarographic behaviour of metal ions in ammonia solution under conditions where a labile complex ammine was formed, much less has been done on the behaviour of the more stable metal ammines. It was expected that platinum(IV) complexes would differ from cobalt(III) complexes in their behaviour at the D.M.E. since the lower oxidation state platinum(II) forms much more stable complexes than cobalt(II). Further, the reduction of cobalt(III) complexes in aqueous solution usually yields the aquated cobalt(II) ion. No such occurrence is possible in the case of platinum, since the ligands attached to the platinum(II) compound will be dependent on those originally present in the platinum(IV) state.

II. Experimental

(*a*) *Apparatus.*—A circuit was arranged to record the waves manually and was based on that described by Kolthoff and Lingane (1939). The voltage was applied across the cell (Kolthoff and Lingane 1939) containing a quiet mercury pool. A saturated potassium chloride bridge similar to that described by Hume and Harris (1943) connected the solution to be electrolysed to an external " reference " (Furness 1952) saturated calomel electrode (S.C.E.). The e.m.f. across the D.M.E. and the S.C.E. was measured by a Cambridge Instrument Co. valve potentiometer. The capillaries used were 10 cm lengths of barometer tubing of uniform internal diameter 0·05 mm. The capillary was connected to the mercury reservoir by " Neoprene " tubing in the way described by Laitinen and Lingane (1939). Under a pressure of 50·0 cm Hg (the height used with both capillaries) the drop time was about 5 sec. The value of m was measured with the mercury dropping in distilled water, and the drop time taken during the actual reductions at the potential where i_d was calculated. A wall-type Leeds and Northrup galvanometer was calibrated to read directly in microamperes by replacing the cell with a known resistance as described by Kolthoff and Lingane (1952).

All measurements were made at 25·0±0·1 °C, the temperature being maintained by a water thermostat. Nitrogen was used to deaerate the solutions and was passed over the surface of the solution while the current-voltage (c-v) curve was being recorded. A tower of chromous chloride, whose affinity for oxygen was studied by Stone (1936), served to remove traces of this gas from the nitrogen.

A Sargent-Heyrovsky Model XII polarograph was operated to obtain continuous curves. The manual plots served for the accurate determination of i_d and $E_{\frac{1}{2}}$.

(*b*) *Materials.*—A.R. KCl and KNO_3 were used. The ammoniacal solutions were obtained by adding the requisite volume of saturated NH_3 solution. Evidence for purity of these reagents follows from the c-v curves for the supporting electrolytes, where the currents recorded for the potentials —0·7, —0·8, —0·9 V *v.* S.C.E. were 0·15, 0·17, 0·20 μA, respectively.

(*c*) *Preparation of Compounds.*—(i) *Tris(ethylenediamine)platinum(IV) Chloride 2,5-Hydrate.* The racemate was prepared as described by Werner (1917).

Crystals of chloroplatinic acid, dried over sodium hydroxide, were dissolved in ethanol, and the solution filtered into a small flask and kept ice-cold. Ethylenediamine was added slowly while shaking the flask. A lumpy pale yellow precipitate of $en.H_2PtCl_6$ was deposited. When all the en(5 mole/atom Pt) had been added the flask was warmed to 75 °C, shaken, and the lumps crushed until the precipitate was greyish white. The alcoholic solution remained a yellow colour. After 1 hr cooling at room temperature, the solution was filtered by suction, and the precipitate washed with a little cold water. The precipitate was dissolved in water at 80 °C, quickly filtered, and the filtrate allowed to cool. The crystals were removed and washed with 50% ethanol and allowed to dry. The substance was recrystallized from hot water and twice from dil. HCl (Found (air-dried material): Pt, 34·2; H_2O, 8·5%. Calc. for $[Pt\ en_3]Cl_4$. $2·5H_2O$: Pt, 34·7; H_2O, 8·0%; Found (dried over P_2O_5): Pt, 37·7%. Calc. for $[Pt\ en_3]Cl_4$: Pt, 37·7%).

(ii) *Hexammineplatinum(IV) Chloride 1-Hydrate and Hexammineplatinum(IV) Nitrate.* These compounds were prepared as by-products in the preparation of chloropentammineplatinum(IV) chloride as described by Tschugajeff (1924).

Ammonium hexachloroplatinate(IV), ammonium carbonate, and 20% ammonia were allowed to stand at room temperature until the yellow colour disappeared. The white residue was filtered, washed with cold water, and dissolved in dil. acetic acid. The solution was filtered and excess conc. HCl added to the filtrate. The white precipitate so formed was recrystallized from HCl solution. The precipitate was again dissolved in water and on the addition of ammonia, yellow amidochlorotetrammineplatinum(IV) chloride was deposited. The solution was filtered and the filtrate heated to remove ammonia. On addition of conc. HCl a white precipitate, mainly the hexammine, was formed. The salt was recrystallized from water and then from HCl

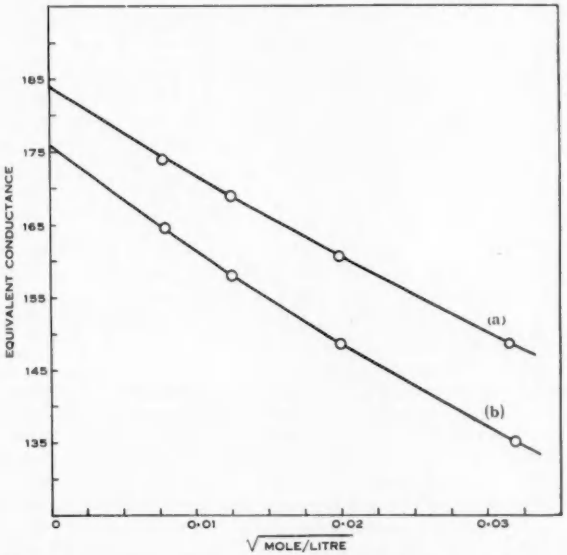

Fig. 1.—Equivalent conductance of (*a*) $[Pt(NH_3)_6]Cl_4$ and (*b*) $[Pt\ en_3]Cl_4$ at 25 °C.

solution (Found: Pt, 42·7; N, 18·3%. Calc. for $[Pt(NH_3)_6]Cl_4.H_2O$: Pt, 42·7; N, 18·4%). This pure product was treated with ammonium carbonate to precipitate the insoluble carbonate. The precipitate was decomposed with conc. HNO_3. The nitrate was only sparingly soluble in HNO_3 solution from which it was recrystallized (Found: Pt, 35·9; N, 25·6%. Calc. for $[Pt(NH_3)_6](NO_3)_4$: Pt, 35·8; N, 25·7%).

(iii) *Bis(ethylenediamine)platinum(II) Chloride.* The procedure of Drew (1932) was followed. Dilute ethylenediamine in water was added dropwise to a warm aqueous solution of potassium tetrachloroplatinate(II). Several minutes were allowed between drops. A yellow precipitate gradually formed which was principally Pt en Cl_2 and possibly containing some $[Pt\ en_2][PtCl_4]$. The precipitate was removed and warmed with excess en until the solution cleared. $[Pt\ en_2]Cl_2$ was precipitated by adding ethanol. The substance was recrystallized from hot water, a small amount of hydrochloric acid being added to the cooled solution (Found: Pt, 50·4; N, 14·4%. Calc. for $[Pt\ en_2]Cl_2$: Pt, 50·5; N, 14·5%).

(iv) *Tetrammineplatinum(II) Perchlorate.* The method of Keller (1946) was followed for the preparation of tetrammineplatinum(II) chloride.

The perchlorate was precipitated by addition of perchloric acid to a cold conc. solution of the chloride. The white crystalline precipitate was recrystallized from boiling water (Found : Pt, 42·1 ; N, 12·2%. Calc. for $[Pt(NH_3)_4](ClO_4)_2$: Pt, 42·2 ; N, 12·1%).

(*d*) *Conductivities of Compounds.*—Since the polarographic reductions proved irreversible, the number of electrons involved in the electrode reactions was determined from the corrected Ilkovic equation. Therefore values of the diffusion coefficients were required. These can be calculated from the equivalent conductivities at infinite dilution. Since the conductivity data available in the literature are limited, conductivities of the compounds were measured.

The apparatus employed consisted of the Wheatstone bridge network fitted with a Wagner earth. The bridge itself was made up of a pair of fixed, equal ratio arms and an adjustable capacity in parallel with the variable resistance. A dip-type conductivity cell with the electrodes lightly platinized made the fourth arm. A.C. 2 kc/s was used.

The temperature of the bath varied by not more than 0·01 °C and the specific conductivity of the water used was calculated to be $1·13 \times 10^{-6}$ mho cm^{-1}. Figure 1 records the results of the measurements.

(*e*) *Polarographic Procedure.*—The experimental procedure was to make up 1 mM solutions of the complex in 0·1M supporting electrolyte and to dilute such solutions of the complex with 0·1M supporting electrolyte to provide the range of concentrations of the complex. Forty ml samples were deaerated for 30 min, then electrolysed. In cases where ammonia was used, the solutions were deaerated before the ammonia was added.

III. Results and Discussion

(i) *The Reduction of Tris(ethylenediamine)platinum(IV) Ion in KCl, KNO_3.*—The reduction of the ion in 0·1M KNO_3 is shown in Figure 2. The four curves represent the residual current, and the reduction of the ion present in the con-

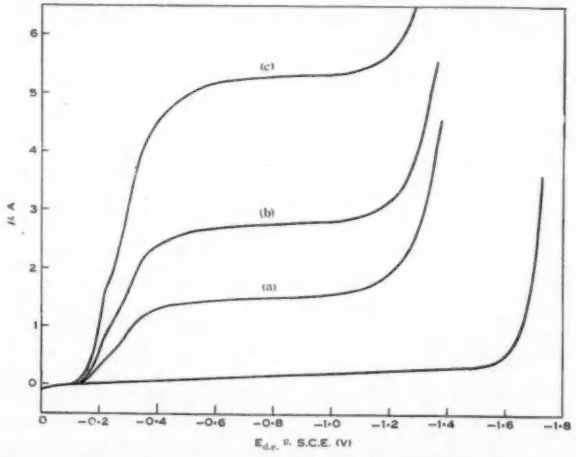

Fig. 2.—The residual current of 0·1M KNO_3 and the reduction of $[Pt\,en_3]^{4+}$ at the concentrations : (*a*) 0·25 mM, (*b*) 0·50 mM, (*c*) 1·00 mM.

centrations 0·25, 0·50, 1·00mM. The proportionality between i_d and C within this concentration range is evident. The reduction of the ion in 0·1M KCl followed a similar course. Table 1 records the characteristics of the reductions.

The diffusion currents in column 2 were obtained by subtracting the residual current from the corresponding limiting current, both measured at —0·9 V

TABLE 1

THE POLAROGRAPHIC REDUCTION OF $[Pt\ en_3]^{4+}$

$m = 1 \cdot 51$ mg sec^{-1}; average drop time $= 4 \cdot 56$ sec at —0·9 V *v.* S.C.E.; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1 \cdot 70$ mg$^{\frac{2}{3}}$ sec$^{-\frac{1}{2}}$; $D^0 = 6 \cdot 71 \times 10^{-6}$ cm^2 sec^{-1}

Concn. (mM)	i_d (μA)	$\frac{i_d}{(Cm^{\frac{2}{3}}t^{\frac{1}{6}})}$	$n_{calc.}$	Recip. Slope of Log Plot		$E_{\frac{1}{2}}$ *v.* S.C.E. (V)	
				1st Wave	2nd Wave	1st Wave	2nd Wave
0·25*	1·33	3·14	1·79	0·15	0·095	—0·20	—0·30
0·50*	2·60	3·07	1·75	0·15	0·11	—0·20	—0·30
1·00*	5·11	3·01	1·72	0·15	0·12	—0·20	—0·30
0·25†	1·33	3·14	1·79	0·15	0·10	—0·19	—0·31
0·50†	2·60	3·07	1·75	0·15	0·13	—0·19	—0·31
1·00†	5·10	3·01	1·72	0·15	0·12	—0·20	—0·31

* Supporting electrolyte 0·1M KNO_3.

† Supporting electrolyte 0·1M KCl.

v. S.C.E. The values for n were calculated from i_d, D^0, using the corrected Ilkovic equation as deduced by Lingane and Loveridge (1950). The diffusion

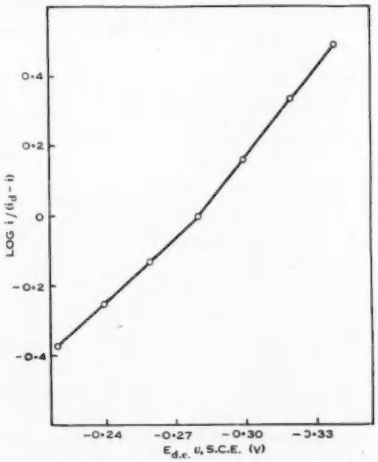

Fig. 3.—Log plot of 1 mM $[Pt\ en_3]^{4+}$ in 0·1M KNO_3.

coefficient was calculated from the equivalent conductance at infinite dilution by means of the Nernst relation,

$$D^0 = 2 \cdot 67 \times 10^{-7}\ \lambda^0/z\ \text{cm}^2\ \text{sec}^{-1}\ \text{at}\ 25\ ^\circ\text{C},$$

where z is the charge on the ion. The value for λ^0 was derived from the conductivity data recorded in Section II (*d*).

On plotting log $i/(i_d-i)$ against $E_{d.e.}$ *v.* S.C.E., points were obtained such that two lines could be drawn intersecting near log $i/(i_d-i)$ equal to zero. Figure 3 represents the log plot of 1mM $[Pt\ en_3]^{4+}$ in 0·1M KNO_3. The reciprocal slopes of such lines for all concentrations are given in Table 1. They show that the reduction was irreversible. Inspection of Figure 2 shows slight inflexions

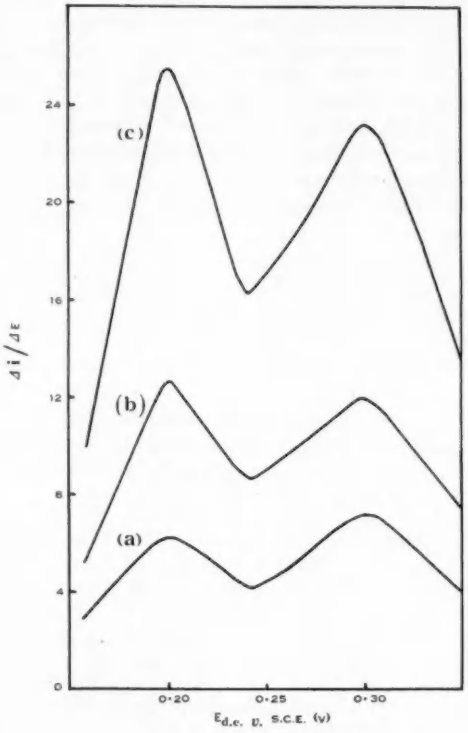

Fig. 4.—The $\Delta i/\Delta E$ curves corresponding to the polarograms in Figure 2.

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in the polarographic waves. On plotting $\Delta i/\Delta E$ *v.* $E_{d.e.}$, the inflexion in the wave was clearly demonstrated by the occurrence of two well-defined peaks separated by approximately 0·1 V, shown in Figure 4.

To support the electrode reactions which follow, solutions of bis(ethylenediamine)platinum(II) chloride in KCl, KNO_3 were studied polarographically. The c-v curves resembled that of the supporting electrolyte in Figure 2, except continuous discharge occurred earlier and in a position, namely, −1·2 V, corresponding to the continuous discharge shown in the reduction of the platinum(IV) ion.

The following electrode reactions are therefore postulated :

$$[Pt\ en_3]^{4+} + e^- \rightarrow [Pt\ en_3]^{3+} \qquad E_{\frac{1}{2}} = -0{\cdot}2\ V, \quad \ldots\ldots\ (1)$$

$$[Pt\ en_3]^{3+} + e^- \rightarrow [Pt\ en_2]^{2+} + en \qquad E_{\frac{1}{2}} = -0{\cdot}3\ V, \quad \ldots\ldots\ (2)$$

$$[Pt\ en_2]^{2+} + 2e^- \rightarrow Pt + 2en \qquad \text{decomp. pot. } c.\ -1{\cdot}2\ V. \quad (3)$$

If at $-1{\cdot}2$ V the complex is being reduced to metallic platinum, this platinum will be in an active state, insoluble in mercury, and being on the surface would lower the overvoltage of hydrogen, leading to its discharge from water at a more positive voltage than on a pure mercury surface. A potential in the continuous discharge region was applied across the cell and after about 30 min several bubbles were observed adhering to the underside of the capillary around the growing drops. During this test, the cell was removed from the water-bath and allowed to cool several degrees to room temperature. This ensured that the solution was unsaturated with respect to nitrogen. Evolution of hydrogen from acid solutions containing small amounts of $[PtCl_4]^{=}$ was studied by Slendyk and Herasymenko (1932).

The postulated initial reduction to platinum(III) appears to proceed irreversibly, indicating that the change is not a simple one-electron addition, but possibly involves a change in the nature of the bonding orbitals used in the formation of the complex. The second reduction (reaction (**2**)) will certainly be irreversible due to the change from an octahedral to a stable planar configuration.

(ii) *The Reduction of Hexammineplatinum(IV) Ion in KCl, KNO_3.*—The information obtained from the c-v curves in KNO_3 is set out in Table 2. D^0 was calculated from conductivity data recorded in Section II (*d*).

TABLE 2

THE POLAROGRAPHIC REDUCTION OF $[Pt(NH_3)_6]^{4+}$ IN 0·1M KNO_3

$m = 1{\cdot}44$ mg sec^{-1} ; average drop time $= 5{\cdot}3$ sec at $-0{\cdot}9$ V *v.* S.C.E. ; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}68$ mg$^{\frac{2}{3}}$ sec$^{-\frac{1}{2}}$; $D^0 = 7{\cdot}16 \times 10^{-6}$ cm^2 sec^{-1}

Concn. (mM)	i_d (μA)	$\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	$n_{calc.}$	Recip. Slope of Log Plot		$E_{\frac{1}{2}}$ *v.* S.C.E. (V)	
				1st Wave	2nd Wave	1st Wave	2nd Wave
0·25	1·47	3·49	1·92	0·16	0·14	—	—0·278
0·50	2·88	3·42	1·88	0·15	0·13	—0·18	—0·275
1·00	5·70	3·39	1·86	0·13	0·10	—0·18	—0·280

The reduction of this ion followed a similar course to the reduction of the tris(ethylenediamine)platinum(IV) ion. It was found that the solubility of hexammineplatinum(IV) chloride was greatly reduced in the presence of chloride ions. However, a sufficient amount dissolved to indicate that the reduction in this medium had the same characteristics as in KNO_3. In both media the same inflexion was present (just as that shown in Fig. 2) so that two straight lines could be drawn in the log plots, and two peaks were obtained in the $\Delta i/\Delta E$ curves similar to those shown in Figures 3 and 4 respectively.

The addition of gelatin had two effects. It shifted the wave to more negative potentials and enhanced the inflexion. These effects were evident from the $\Delta i/\Delta E$ curve for the reduction of 1·0mM $[Pt(NH_3)_6]^{4+}$ in 0·1M KNO_3 and 0·01 per cent. gelatin, where the peaks occurred at −0·25 and −0·43 V.

Solutions of tetrammineplatinum(II) perchlorate were polarographed in KCl and KNO_3. The c-v curves obtained resembled the curve for the supporting electrolyte except that continuous discharge occurred from *c.* −1·3 V onwards.

The following electrode reactions which correspond to those given for the reduction of $[Pt\ en_3]^{4+}$ are postulated :

$$[Pt(NH_3)_6]^{4+} + e^- \rightarrow [Pt(NH_3)_6]^{3+} \qquad E_{\frac{1}{2}} = -0{\cdot}18\ V, \quad \ldots\ldots\ (4)$$

$$[Pt(NH_3)_6]^{3+} + e^- \rightarrow [Pt(NH_3)_4]^{2+} + 2NH_3 \qquad E_{\frac{1}{2}} = -0{\cdot}28\ V, \quad \ldots\ldots\ (5)$$

$$[Pt(NH_3)_4]^{2+} + 2e^- \rightarrow Pt + 4NH_3 \qquad \text{decomp. pot. } c.\ -1{\cdot}3\ V,$$
$$Pt + H_2O + e^- \rightarrow Pt + \tfrac{1}{2}H_2 + OH^-. \qquad \ldots\ldots\ (6)$$

(iii) *The Reduction of the Ions* $[Pt\ en_3]^{4+}$, $[Pt(NH_3)_6]^{4+}$ *in* KNO_3 *and Ammonia.*—The reduction of the former ion at several concentrations is shown in Figure 5. The form of the wave for the reduction of the latter ion was similar.

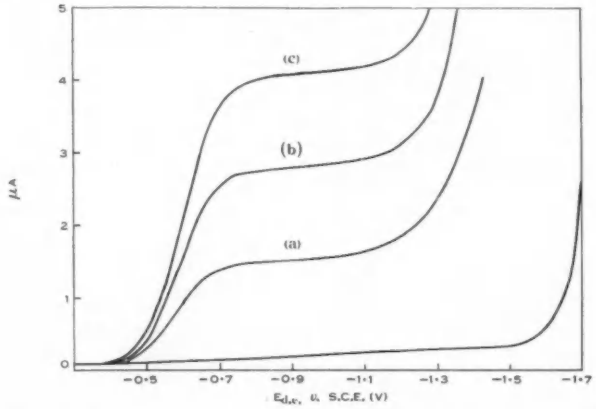

Fig. 5.—The residual current of 0·1M KNO_3 and 1N NH_4OH, and the reduction of $[Pt\ en_3]^{4+}$ at the concentrations (*a*) 0·25 mM, (*b*) 0·50 mM, (*c*) 0·75 mM.

Data obtained are supplied in Tables 3 and 4. It was assumed that the diffusion coefficients in dilute ammonia were not appreciably different from those in the aqueous media.

From Figure 5 it is noted that no trace of any inflexion is present. This is corroborated by the log plots and $\Delta i/\Delta E$ curves which contain one line and one peak respectively. Therefore the reduction in each case was an irreversible two-electron addition. Continuous discharge occurred at the same positions as for the corresponding complexes in aqueous solution.

The shift in half-wave potential, when ammonia is present, may be due to the formation of a new species in the solution. It is known that hexammineplatinum(IV) ion can function as a weak acid (Emeléus and Anderson 1952). The acidity is due to the dissociation,

$$[Pt(NH_3)_6]^{4+} \rightleftharpoons [Pt(NH_3)_5NH_2]^{3+} + H^+.$$

The equilibrium will be shifted towards the right in alkaline media. To test whether the shift in potential is due to the presence of the amidopentammineplatinum(IV) ion, a series of experiments on the reduction of this ion in alkaline buffers is being carried out. The results will be reported in a later paper in this series.

TABLE 3

THE POLAROGRAPHIC REDUCTION OF $[Pt\,en_3]^{4+}$ IN 0·1M KNO_3, 1N NH_4OH

$m = 1{\cdot}51$ mg sec^{-1}; average drop time $= 4{\cdot}53$ sec at $-0{\cdot}9$ V *v.* S.C.E.; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}69$ $mg^{\frac{2}{3}}$ $sec^{-\frac{1}{2}}$; $D^0 = 6{\cdot}71 \times 10^{-6}$ cm^2 sec^{-1}

Concn. (mM)	i_d (μA)	$\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	$n_{calc.}$	Recip. Slope of Log Plot	$E_{\frac{1}{2}}$ *v.* S.C.E. (V)
0·25	1·32	3·12	1·78	0·10	−0·570
0·50	2·59	3·06	1·75	0·11	−0·588
0·75	3·87	3·05	1·74	0·12	−0·600

TABLE 4

THE POLAROGRAPHIC REDUCTION OF $[Pt(NH_3)_6]^{4+}$ IN 0·1M KNO_3, 1N NH_4OH

$m = 1{\cdot}44$ mg sec^{-1}; average drop time $= 5{\cdot}2$ sec at $-0{\cdot}9$ V *v.* S.C.E.; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}68$ $mg^{\frac{2}{3}}$ $sec^{-\frac{1}{2}}$; $D^0 = 7{\cdot}16 \times 10^{-6}$ cm^2 sec^{-1}

Concn. (mM)	i_d (μA)	$\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	$n_{calc.}$	Recip. Slope of Log Plot	$E_{\frac{1}{2}}$ *v.* S.C.E. (V)
0·25	1·46	3·48	1·91	0·080	−0·534
0·50	2·86	3·41	1·87	0·083	−0·540
0·75	4·31	3·42	1·88	0·089	−0·547

Regardless of the nature of the original reducible species, a two-electron addition will result in the formation of the tetrammineplatinum(II) ion. Hence the overall reaction in ammoniacal solution may be represented by :

$$[Pt(NH_3)_6]^{4+} + 2e^- \rightarrow [Pt(NH_3)_4]^{2+} + 2NH_3, \quad \ldots\ldots\ldots (7)$$

$$\left.\begin{aligned} &[Pt(NH_3)_4]^{2+} + 2e^- \rightarrow Pt + 4NH_3, \\ &Pt + H_2O + e^- \rightarrow Pt + \tfrac{1}{2}H_2 + OH^-. \end{aligned}\right\} \quad \ldots\ldots\ldots (8)$$

The behaviour of tris(ethylenediamine)platinum(IV) ion in ammonia which follows closely that of the hexammine ion will also be studied further.

IV. Acknowledgments

The authors express their thanks to Research Professor F. N. Lahey and Mr. B. Hughes for the determinations of nitrogen in the compounds studied. They also wish to thank Associate Professor I. Lauder and Mr. I. Wilson for assistance with the conductivity measurements.

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POLAROGRAPHY OF SOME COORDINATION COMPOUNDS OF PLATINUM

II. IONS OF THE HALOGENO-PENTAMMINEPLATINUM(IV) TYPE

By J. R. HALL* and R. A. PLOWMAN*

[*Manuscript received November* 1, 1954]

Summary

The hydroxo- and chloropentammineplatinum(IV) ions have been studied in potassium chloride, potassium nitrate, and potassium nitrate plus ammonia. Bromopentammineplatinum(IV) ion was studied in potassium chloride. All the ions were reduced irreversibly, producing waves with i_d proportional to concentration. The wave heights corresponded to two-electron reductions. The effect of substituting an electronegative group for an ammonia molecule in the hexammineplatinum(IV) ion was to shift the half-wave potential in the order

$$-Br < -Cl < -NH_3 < -OH.$$

Continuous discharge began in every case at *c.* $-1{\cdot}3$ V and was assumed due to the evolution of hydrogen consequent to the further reduction of the complex to platinum metal.

I. INTRODUCTION

In Part I of this series (Hall and Plowman 1955), ions of the hexammineplatinum(IV) type were studied. With the information contained in the present paper further support for the initial assumptions can be gained.

II. EXPERIMENTAL

(*a*) *Apparatus and Materials.*—The apparatus previously described (p. 159) was employed. A.R. KCl and KNO_3 were used.

(*b*) *Preparation of Compounds.*—(i) *Chloropentammineplatinum(IV) Nitrate 1-Hydrate.* The chloride was first prepared by Tschugajeff (1924, p. 19).

The procedure was outlined in Part I of this series (loc. cit.), under the heading for the preparation of hexammineplatinum(IV) chloride, Section II (*c*). The yellow amidochlorotetrammineplatinum(IV) chloride obtained during the preparation was dissolved in acetic acid and chloropentammineplatinum(IV) chloride was precipitated on adding conc. HCl. The chloride formed analysed for one molecule water of crystallization. Since this compound slowly loses ammonia on standing, the nitrate, which is quite stable, was prepared. The chloride was dissolved in the minimum amount of water and conc. HNO_3 added. The white precipitate was recrystallized twice from HNO_3 solution. The nitrate also analysed for one molecule water of crystallization (Found: Pt, 37·5; N, 21·6; Cl, 6·7; H_2O, 3·9%. Calc. for $[Pt(NH_3)_5Cl](NO_3)_3H_2O$: Pt, 37·6; N, 21·6; Cl, 6·8; H_2O, 3·5%).

(ii) *Hydroxopentammineplatinum(IV) Chloride 1-Hydrate.* This compound was prepared by Tschugajeff (1924, p. 26).

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A quantity of amidochlorotetrammineplatinum(IV) chloride was suspended in 3% sodium hydroxide and heated at the b.p. until the solution was clear. The solution was filtered, cooled, and acidified with HCl. The precipitate was recrystallized from water and from HCl solution, pale cream crystals being obtained (Found: Pt, 46·3; N, 16·6; Cl, 25·0%. Calc. for $[Pt(NH_3)_5OH]Cl_3H_2O$: Pt, 46·3; N, 16·6; Cl, 25·2%).

(iii) *Bromopentammineplatinum(IV) Bromide.* Tschugajeff's (1924, p. 30) procedure was followed.

Ammonium hexabromoplatinate(IV), disodium hydrogen phosphate, and 20% ammonia were mixed and heated almost to the b.p. The red colour soon disappeared, giving way to a pale yellow precipitate which was mainly bromopentammineplatinum(IV) phosphate. The phosphate was dissolved in conc. HBr (sp. gr. 1·45), and on careful further addition of the same acid the bromide was precipitated (Found: Pt, 32·5; N, 11·9%. Calc. for $[Pt(NH_3)_5Br]Br_3$: Pt, 32·5; N, 11·7%). On standing, the dry salt darkened in colour due to loss of ammonia forming $[Pt(NH_3)_4Br_2]Br_2$.

(*c*) *Conductivities of Compounds.*—The conductivities of the hydroxo- and chloropentammineplatinum(IV) salts were studied at various dilutions. The apparatus previously described by Hall and Plowman (1955) was used. Figure 1 records the results of the measurements.

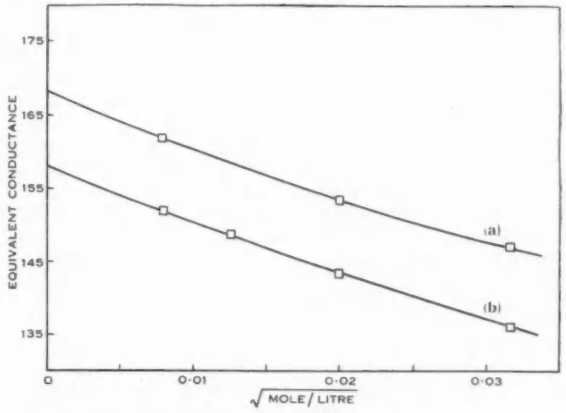

Fig. 1.—Equivalent conductance of (*a*) $[Pt(NH_3)_5OH]Cl_3$ and (*b*) $[Pt(NH_3)_5Cl](NO_3)_2$ at 25° C.

III. Results and Discussion

(i) *The Reduction of the Hydroxopentammineplatinum(IV) Ion.*—Figure 2 represents the reduction of the ion in 0·1M KNO_3. The reduction in potassium chloride and ammoniacal solutions followed a similar course. Table 1 lists the data obtained from the current-voltage (c-v) curves.

In each medium an irreversible two-electron addition occurred. A well-defined diffusion current region was followed by continuous discharge beginning at *c.* −1·3 V. The value given for the diffusion coefficient was estimated from conductivity data recorded earlier.

(ii) *The Reduction of the Chloropentammineplatinum(IV) Ion.*—The ion was reduced in the three media previously mentioned. In 0·1M KNO_3, the reduction occurred at positive potentials *r.* the S.C.E., and only a small residual current

region was present before the anodic dissolution wave of mercury. In KCl and ammoniacal solutions, the anodic dissolution wave and the reduction step of the ion practically merged. Maxima occurred in all three media and were removed by the addition of 0·01 per cent. gelatin. Diffusion current regions were obtained

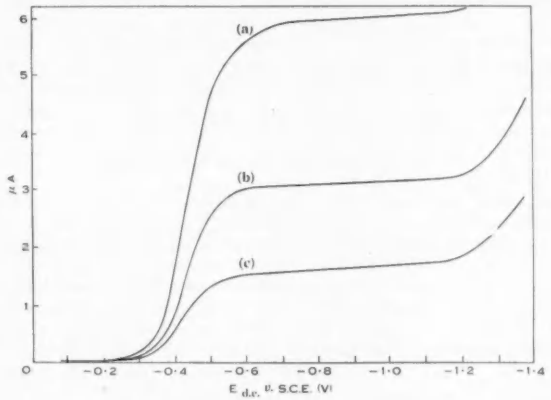

Fig. 2.—Polarograms of $[Pt(NH_3)_5OH]^{3+}$ at the concentrations: (*a*) 1·00 mM in 0·1M KNO_3; (*b*) 0·50 mM; (*c*) 0·25 mM.

prior to continuous discharge which occurred at *c.* −1·3 V. Table 2 sets out the data available from the c-v curves.

Evaluation of n showed that the reduction was a two-electron change. The log plots indicated an irreversible process. The reduction waves in KCl

TABLE 1

THE POLAROGRAPHIC REDUCTION OF $[Pt(NH_3)_5OH]^{3+}$

$m = 1·44$ mg sec^{-1}; average drop time = 5·2 sec at −0·9 V *v.* S.C.E.; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1·68$ mg$^{\frac{2}{3}}$ sec$^{-\frac{1}{2}}$
$D^0 = 8·22 \times 10^{-6}$ cm^2 sec^{-1}

Concn. (mM)	i_d (μA)	$\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	$n_{calc.}$	Recip. Slope of Log Plot	$E_{\frac{1}{2}}$ *v.* S.C.E. (V)
0·25*	1·50	3·58	1·82	0·086	−0·433
0·50*	2·99	3·56	1·81	0·087	−0·438
1·00*	5·90	3·52	1·79	0·102	−0·442
0·25†	1·53	3·65	1·86	0·091	−0·471
0·50†	2·98	3·55	1·80	0·097	−0·475
1·00†	5·91	3·52	1·79	0·106	−0·480
0·25‡	1·53	3·65	1·86	0·079	−0·558
0·50‡	3·01	3·59	1·82	0·085	−0·560
0·75‡	4·48	3·56	1·81	0·090	−0·560

* Supporting electrolyte 0·1M KNO_3.
† Supporting electrolyte 0·1M KCl.
‡ Supporting electrolyte 0·1M KNO_3, 1N NH_4OH.

and ammoniacal solutions were influenced by the anodic dissolution of mercury, so that log plots and half-wave potentials have no significance in these cases.

(iii) *The Reduction of the Bromopentammineplatinum(IV) Ion.*—This ion was reduced in 0·1M KCl at a concentration equal to 1mM. The addition of gelatin was necessary to suppress a maximum. The wave started from zero applied

TABLE 2

THE POLAROGRAPHIC REDUCTION OF $[Pt(NH_3)_5Cl]^{3+}$

$m = 1 \cdot 51$ mg sec^{-1}; average drop time = 4·5 sec at −0·9 V *v.* S.C.E.; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1 \cdot 69$ mg$^{\frac{2}{3}}$ sec$^{-\frac{1}{2}}$; $D^0 = 7 \cdot 71 \times 10^{-6}$ cm^2 sec^{-1}

Concn. (mM)	i_d (μA)	$\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	$n_{calc.}$	Recip. Slope of Log Plot	$E_{\frac{1}{2}}$ *v.* S.C.E. (V)
0·25*	1·38	3·27	1·73	0·072	0·058
0·50*	2·96	3·50	1·85	0·088	0·055
1·00*	5·70	3·37	1·78	0·092	0·055
0·25†	1·38	3·27	1·73	—	—
0·50†	2·88	3·41	1·81	—	—
1·00†	5·64	3·34	1·77	—	—
0·25‡	1·37	3·24	1·72	—	—
0·50‡	2·90	3·43	1·82	—	—
0·75‡	4·40	3·47	1·84	—	—

* Supporting electrolyte 0·1M KNO_3, 0·01% gelatin.
† Supporting electrolyte 0·1M KCl, 0·01% gelatin.
‡ Supporting electrolyte 0·1M KNO_3, 1N NH_4OH, 0·01% gelatin.

potential and attained a diffusion current region before continuous discharge at *c.* −1·3 V. The magnitude of the diffusion current was comparable with that for the chloropentammine ion, so that a two-electron change can be assumed.

The electrode reactions can be written in the general form :

$$[Pt(NH_3)_5X]^{3+} + 2e^- \rightarrow [Pt(NH_3)_4]^{2+} + NH_3 + X^-, \quad \ldots\ldots (1)$$

$$\left.\begin{aligned} [Pt(NH_3)_4]^{2+} + 2e^- &\rightarrow Pt + 4NH_3, \\ Pt + H_2O + e^- &\rightarrow Pt + \tfrac{1}{2}H_2 + OH^-. \end{aligned}\right\} \quad \ldots\ldots\ldots (2)$$

IV. CONCLUSION

The reduction of halogeno-pentammineplatinum(IV) ions differed from the reduction of the hexammine- and tris(ethylenediamine)platinum(IV) ions in that only two-electron changes to platinum(II) salts were observed. The $\Delta i/\Delta E$ curves showed only one peak. The reduction of all these salts, however, was similar in that it proceeded irreversibly, as might be expected for a change from an octahedral to a planar configuration.

Halogeno-pentammine salts gave a continuous discharge current at the same potential as that obtained in the reduction of hexammineplatinum(IV) ion. This seems to indicate a common process in both cases.

The half-wave potential occurred at more positive values when an ammonia group of hexammineplatinum(IV) ion was replaced by chlorine or bromine.

The shift however was to a more negative value when ammonia was replaced by a hydroxyl group. The effect of the different groups on $E_{\frac{1}{2}}$'s is represented by

$$-\mathrm{Br} \leqslant -\mathrm{Cl} < -\mathrm{NH_3} < -\mathrm{OH}.$$

In the presence of ammonia the $E_{\frac{1}{2}}$'s shift to more negative values. This effect is being investigated further and the results will be reported in a later paper in this series.

V. Acknowledgments

The authors express their thanks to Research Professor F. N. Lahey and Mr. B. Hughes for the determinations of nitrogen in the compounds studied. The authors also wish to thank Associate Professor I. Lauder and Mr. I. Wilson for assistance with the conductivity measurements.

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A RADIOACTIVE TRACER STUDY OF THE BEHAVIOUR OF LONG CHAIN ORGANIC MOLECULES ON SOLID SURFACES

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Summary

The adsorption and possible mechanisms for the surface transport of stearic acid and some of its derivatives on solids have been investigated using radioactive tracers. Mono- and multimolecular layers of these compounds were deposited on quartz glass, mica, and metal specimens, which were then held at various temperatures for a short period. The resulting changes in amount and distribution of activity were determined by autoradiography or an appropriately designed Geiger tube.

On unreactive surfaces such as platinum or quartz glass the pure acid is only weakly adsorbed and thermal desorption, in general, readily occurs, especially of layers deposited on an initial monolayer. Layers of copper or calcium soaps on all surfaces, either deposited as such or formed *in situ*, are very much more stable. There is also some evidence that desorption is favoured by the presence of water vapour. Both pure acid and soap layers have some resistance to mechanical abrasion, but none to dissolution by hot benzene unless the adsorption involves a chemical bond.

Part *B* of the present paper describes an experimental search for a long-range surface diffusion, using the same surfaces and adsorbates. It is shown that, under favourable conditions, material desorbed from one part of a surface will readsorb elsewhere after movement over considerable distances in the vapour phase. This mechanism may account for some examples of apparent surface diffusion reported by earlier workers. If, however, this vapour phase transport is suppressed, then no evidence can be detected of a true surface diffusion over macroscopic distances.

A. ADSORPTION AND DESORPTION

I. INTRODUCTION

Long chain organic molecules containing one or more polar groups adsorb readily on most solid surfaces. If the layers so formed are one molecule thick, the chains are usually close packed and orientated approximately normal to the surface. These facts have been deduced from several experimental approaches, most of which, however, are indirect or of limited sensitivity. Whilst the structures and properties of complete monolayers and multilayers are therefore well established, less is known about the behaviour of adsorbed material at lower surface concentrations. Recently this problem has been attacked by radioactive tracers, incorporated either into the long chain molecules themselves or the solid surfaces, with promising results.

The extent of true chemical interaction between adsorbed layers of long chain fatty acids, alcohols, or esters, and metal surfaces was determined by

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Bowden and Moore (1951), who adsorbed these compounds from benzene solution on radioactive foils, and subsequently measured the activity transferred to the solution and to an extract obtained by washing the foils with fresh solvent. It was found that the acids react continuously on zinc, copper, and cadmium surfaces with dissolution of reaction products into the surrounding liquid, but there was no evidence of a similar action on gold or platinum. The technique, however, does not give a direct picture of the amount of long chain material adsorbed sufficiently strongly to resist solution in benzene, nor does it provide any information on purely physical adsorption. Preliminary experiments from the latter viewpoint have been reported by Hensley, Skinner, and Suter (1952), Beischer (1951, 1953), and Rideal and Tadayon (1954), using stearic acid labelled with ^{14}C in the carboxyl group.

Hensley deposited thin layers of the acid (by solvent evaporation) on steel surfaces and, after these had been immersed in aqueous detergents, traces of activity were still present. Autoradiographs showed that this residue was irregularly distributed. The work described by Beischer was more fundamental and used mono- and multilayers of stearic acid, or a metallic stearate. These were aged for a known time, and then an estimate was made of both the free stearic acid which could be removed and the stearate which remained. Removal of free acid was effected either by evaporation *in vacuo* or by benzene, though apparently some stearate was detached as well. Any undesorbed stearate was estimated by autoradiography. The chief conclusions were that adsorption is very weak on platinum, Pyrex glass, quartz glass, or the basal plane of mica, and strong with definite chemical reaction on copper, lead, aluminium, or surfaces of mica other than the basal plane. Measurements of adsorption were made by Rideal and Tadayon, who deposited layers on a specimen of one material and then determined the extent of transfer at various temperatures to a specimen of a second material pressed into contact. After some time an equilibrium state was reached and from the partition of stearic acid between the two surfaces the adsorption bonds to each could be compared. The results were generally in harmony with those of Beischer, except for the observation that stearic acid was strongly adsorbed on platinum.

The experiments to be described here were similar to the above work and included a more detailed study of desorption by heating, mechanical abrasion, or the solvent action of benzene. Layers of radioactive stearic acid or metal stearate were prepared by the Langmuir-Blodgett technique, or in a few instances by retraction, and their properties determined from autoradiographs. Reactive surfaces are again shown to exhibit little or no desorption, and metal stearate layers to be more stable than those of pure acid alone. In addition, there is some evidence that desorption behaviour is influenced by the presence of water vapour.

II. Experimental

Stearic acid containing $1\frac{1}{2}$ per cent. of $C_{17}H_{35}{}^{14}COOH$ from the A.E.R.E. was used without further purification. Solutions were made up in redistilled benzene for the trough work, and in very carefully purified cetane for the experiments on retraction. The deposition of Langmuir-Blodgett layers was carried

out by standard methods using castor oil or oleic acid as piston oil. Layers of the pure acid were obtained from a conductivity water surface, and mixed acid-stearate layers from M/2000 $CuCl_2$ or, for one set of experiments only, M/10,000 $CaCl_2$ adjusted to a pH of 9. The pH of the cupric chloride solution was *c.* 5·3, at which value about 70 per cent. of a stearic acid layer spread on its surface should be converted to copper stearate (Sanders and Spink 1955). On the calcium solution the conversion to stearate was probably almost complete. To ensure that the copper stearate layers would deposit evenly, a reduced surface pressure was applied by substituting castor oil for oleic acid.

For the preparation of monolayers by the retraction principle, a technique due to Zisman, Bigelow, and Pickett (1946) was used. One drop of a solution of the long chain compound in a non-polar hydrocarbon is placed on a clean surface. The drop then usually spreads over the whole area, followed by adsorption of the long chain polar molecules at the solution-solid interface. When a complete orientated monolayer has formed the surface ceases to be wetted by the solution, which accordingly retracts into one or more drops. These are removed by blotting, leaving the required monolayer on the surface.

The behaviour of deposited layers was studied on copper, platinum, and mica surfaces, and retracted layers on copper and mica only. These surfaces were formed by preparing both sides of thin metal slips or, in the case of mica, by cleavage. The copper and platinum were commercial high purity material and the mica (a good quality muscovite type) came from central Australia. As in Beischer's work, a series of fine scratches was made on both sides of each mica slip in order to expose non-basal planes, but otherwise there was no delay between cleaving and deposition or retraction.

Under atmospheric conditions it is impossible to prepare an absolutely clean metal surface ; oxidation may occur during the cleaning operation itself, and is followed by the adsorption of water vapour together with traces of other forms of airborne contamination. As these modify the surface properties of most metals very considerably, experiments with intentionally added surface layers must be designed so that this prior contamination is known, reproducible, and kept to a minimum. For the work described here the metals were cleaned by very simple techniques and then, as in the work of Brockway and Karle (1947), a number of control specimens examined in the electron-diffraction camera to determine the nature of the surfaces so formed.

Platinum was cleaned in hot chromic acid, thoroughly rinsed in conductivity water, and briefly flamed. The resulting surface gave a diffraction pattern characteristic of the pure metal alone, though with specimens kept in the atmosphere, a slight adsorption of water vapour would be expected. The copper specimens were prepared by abrasion with 320 grade carborundum paper under tap-water, rinsing in conductivity water, and, where necessary, drying in a current of warm air. This produces a hydrophilic surface giving the diffraction pattern of cuprous oxide, Cu_2O. On the specimens actually used there would be naturally a heavy adsorption of water as well. Abrasion under ethanol yielded substantially the same result. An examination was also made

of copper surfaces which had been immersed for some minutes in boiling conductivity water, or cupric chloride solution. These reagents attack the metal very rapidly with the formation of a thick visible corrosion layer also identified as Cu_2O.

The slight surface roughness left by these methods of cleaning did not interfere with the deposition of layers from the trough, Langmuir-Blodgett layers being able to bridge over small surface furrows. The surface was, however, unsatisfactory for the retraction work. The cleaned metal specimens were therefore lightly polished, using alumina on cloth followed by cloth alone, and in the case of copper the retraction technique was then successful.

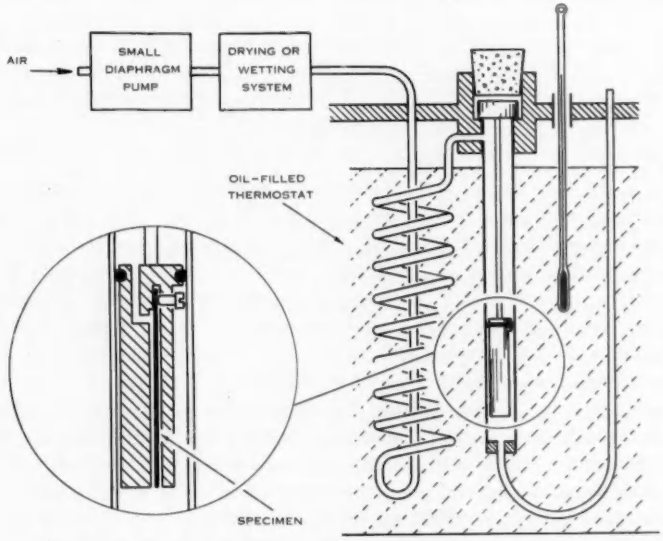


Fig. 1.—Thermostat arrangement for thermal desorption experiments.

For the study of thermal desorption the specimens were heated under carefully controlled conditions. The apparatus is shown in Figure 1, and consists of an oil-filled thermostat with provision for passing a slow current of air over the specimen. Before reaching the specimen this air supply is passed through a drying, or a wetting, system, and a long temperature-equalizing coil which is also immersed in the thermostat tank. Thus the specimen and the air supply are in good thermal equilibrium with the oil. Drying is effected by a phosphorus pentoxide column in series with a liquid air trap, and wetting by bubbling the air through conductivity water. The specimen is mounted in the special holder, illustrated in section, which can be inserted into an enlarged section of the air line. A silicone rubber seal ensures that the air is constrained to pass through a narrow channel and impinge on one side only of the specimen. Specimens were usually annealed for 1 hr at 81 °C, which is above the melting

point of pure stearic acid (69 °C), but below the softening range of copper or calcium stearate.

Investigations were also made into desorption by solvent action and by mechanical abrasion. Deposited layers were exposed to benzene by immersing the specimens in a large volume of the pure boiling solvent for 5 minutes. This experiment was carried out on freshly deposited layers and also on layers which had been heated in the thermal desorption apparatus. The abrasion took the form of a gentle one-directional rubbing with cotton wool, and was done on freshly deposited layers only.

All specimens in the deposition work were immersed to a convenient depth in the trough before the long chain compounds were spread on the surface. Langmuir-Blodgett layers then deposited on the initial withdrawal, and subsequently on both immersion and withdrawal. To obtain a comparison between the properties of long chain molecules in direct contact with the solid and those in superposed layers, it was arranged that part of the specimen surface should receive only the initial monolayer and another part three layers. Autoradiographs taken after desorption treatment thus show the behaviour of both the initial and the superposed layers, which can then be compared directly. In addition, the *absolute* extent of desorption was estimated by comparison with autoradiographs of control specimens not subject to desorption.

The autoradiographs were made by sandwiching each specimen between sheets of X-ray film, and developing these in the normal way after an exposure time of *c.* 60 hours. Intimate contact of the emulsions with the radioactive specimen surfaces was ensured by clamping the sandwich between two flat rigid brass disks. A " Neoprene " ring surrounding the sandwich excluded light and moisture. The entire assembly was kept below 0 °C during the exposure period, in order to suppress any surface processes which might otherwise modify the autoradiographs. ^{14}C emits only soft β-rays and the autoradiograph images consequently show excellent resolution. With the above exposure time the contrast range of the film covers a range of tracer concentration from three monolayers down to fractions of a complete monolayer, and qualitative estimates of desorption are thus easily made. The density is also a function of back-scattering from the specimen, but allowance for this factor is automatically made when autoradiographs from desorption and control specimens of the same material are compared. Additional check experiments showed that no radioactive contamination could be picked up by a specimen whilst in the thermostat, or a film whilst in the cell.

Finally, the Langmuir-Blodgett layers themselves were examined, by electron diffraction, to obtain independent data about their structure on metal substrates. Good patterns were obtained from stearic acid on platinum and copper, and copper stearate on platinum, but no long chain patterns were observed from copper stearate on copper. This failure may be attributed to the heavy oxidation of copper by the cupric chloride solution, together with excessive surface roughness.

III. Results

The observations on desorption, and the electron-diffraction data, are summarized in Table 1. In most experiments the autoradiographs revealed either negligible or almost complete desorption; intermediate behaviour was

Table 1

DESORPTION BEHAVIOUR ETC. OF LONG CHAIN ORGANIC COMPOUNDS ON SOLID SURFACES

Symbols indicate state of desorption thus: ○ almost complete; ◓ partial; ● little or none. Figures in brackets refer to corresponding autoradiographs in Plates 1 and 2. Subscripts i and ii with reference to thermal desorption of stearic acid from platinum indicate the initial monolayer and subsequent layers respectively

Surface	Property Studied	Nature of Adsorbed Material			
		Stearic Acid Applied by:		Langmuir-Blodgett Layers Composed Partly of the Stearates of:	
		Retraction Technique	Langmuir-Blodgett Technique	Copper	Calcium
Copper	Effect of 1 hr heating at 81 °C in air-stream	Wet ● (7) Dry ●	● (5) ●	● ●	● (Semi-dry)
	Resistance to: Abrasion Hot benzene		● ◓	● ◓ (6)	
	Electron diffraction data		Weak soap pattern	No pattern	
	Vapour-phase transport ?		Very slight	Very slight (12)	
Platinum	Effect of 1 hr heating at 81 °C in air-stream	Wet Dry	◓ (3(*a*)) ○ ● (3(*b*)) ○ii	◓ (4) ●	● (Semi-dry)
	Resistance to: Abrasion Hot benzene		● ○	● ○	
	Electron diffraction data		Free acid pattern	Soap pattern	
	Vapour-phase transport ?		Yes	Yes (11)	
Mica	Effect of 1 hr heating at 81 °C in air-stream	Wet ○ Dry ○	○ (1) ○	◓ (2) ●	◓ (Semi-dry)
	Resistance to: Abrasion Hot benzene		◓ ○	◓ ○	
	Vapour-phase transport ?		Yes (9)	Yes (10)	

rare. The results are therefore expressed by the use of three symbols, according to the amount of long chain material remaining on a surface after a given treatment. Typical examples of desorption etc. are then illustrated in Plates 1 and 2.

The results obtained with stearic acid on mica substantially reproduce the observations of Beischer (1951). Very weak attachment to the basal plane contrasted sharply with marked retention wherever non-basal planes were exposed at the specimen edges and intentionally made scratches. However, copper and calcium stearates were resistant to thermal desorption on either type of plane, especially under conditions of very dry ventilation. Both the pure acid and copper stearate showed some resistance to abrasion, but none to dissolution by benzene.

All the adsorbed layers on copper were very stable. Thermal desorption was negligible, resistance to abrasion good, and an appreciable fraction of deposited long chain material could not be removed by hot benzene. This similarity in behaviour of the acid and the stearates supports the view that stearic acid adsorbed onto copper may be converted *in situ* to copper stearate. This is further confirmed by the electron-diffraction observations, which in all cases recorded a weak soap pattern from layers of stearic acid on copper.

On platinum the thermal desorption properties of pure acid and metal stearate are different. Stearic acid molecules are stable only if in direct contact with the platinum and those in superposed layers desorb readily, whilst copper stearate molecules are equally stable in both positions. Resistance to thermal desorption was in each instance greater under very dry conditions. It is also shown that the adsorption forces between these long chain compounds and platinum are sufficient to resist light mechanical abrasion, though not dissolution by benzene. Reaction is of course not possible, and the diffraction patterns obtained from layers on platinum were characteristic of either acid or stearate as deposited.

In addition to the observation that thermal desorption may be reduced by very dry ventilation, it was noted with copper and platinum surfaces that desorption of stearate layers by solvent action is less marked with annealed than freshly deposited layers. This point is illustrated in autoradiographs (Plate 1, Figs. 6 (*a*) and 6 (*b*)) which refer to copper.

The data from deposited layers of calcium stearate on all surfaces were obtained in preliminary work, where the ventilation air supply was dried over phosphorus pentoxide only. The results are generally in harmony with those from copper stearate and are quoted in support.

IV. Discussion

The radioactive tracer technique is shown to be a very convenient and direct means of investigating the desorption process, and by using a range of adsorbed layers and specimen surfaces these experiments have given data for systems of both physically and chemically adsorbed molecules. It has also been possible to correlate desorption behaviour with the thermal stability of an adsorbate in bulk. Physical adsorption is provided by mica or platinum

surfaces, and these results will be discussed first. We shall then consider the chemical reaction and adsorption which takes place on copper surfaces, and lastly the influence of water on the desorption process in general.

(*a*) *Physical Adsorption*

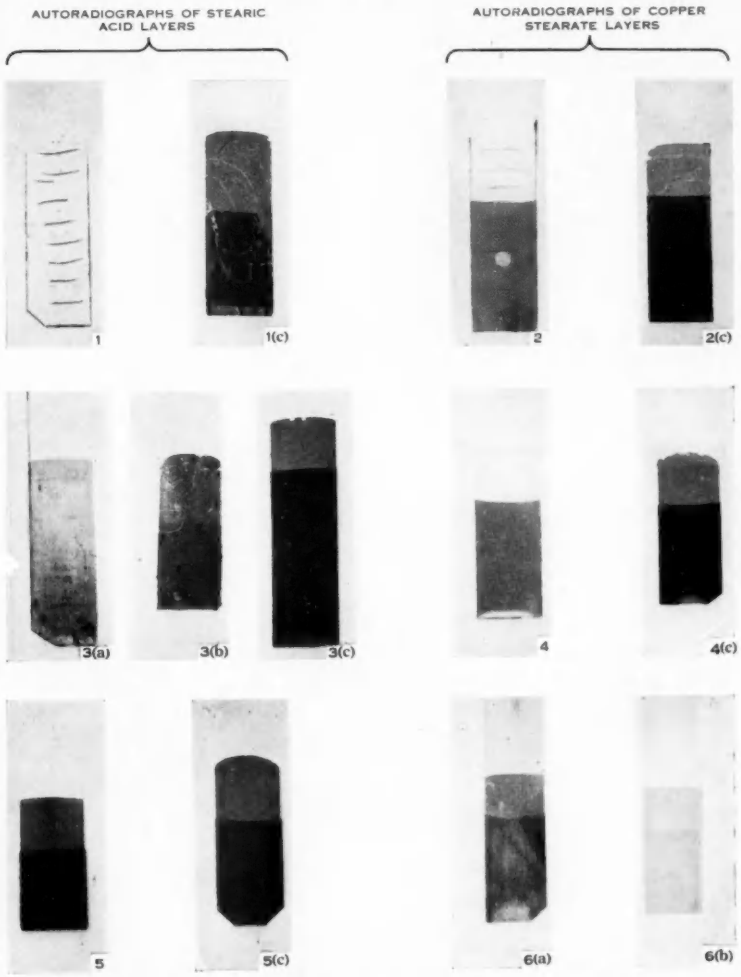
The autoradiographs show that physically adsorbed layers of stearic acid undergo complete desorption from the basal plane of mica, at atmospheric pressure, when heated to only 12 °C above the melting point of the acid in bulk. On platinum the effect is not as marked, which suggests that the bonding of the polar group with a metal is stronger than with a dielectric. It is interesting to find that Brunauer (1943) reaches the same conclusion from a theoretical consideration of physical adsorption by dipole-induced dipole forces. As the platinum was free from oxide or other gross contamination, the polar group of the acid would be able to approach the metal lattice very closely and these electrostatic image forces should become appreciable. The initial monolayer is thus attached by a strong physical adsorption, but as the bond to the next layer can be only a weak van der Waals attraction, it is not surprising that superposed layers desorb readily. On mica it is probable that the adsorption arises chiefly from electrostatic bonding at the relatively sparse K atoms of the surface, and any image forces will be extremely weak. Although this is sufficient to allow of Langmuir-Blodgett deposition it offers very little resistance to thermal desorption. Where non-basal planes are exposed, however, the acid is chemisorbed and desorption becomes negligible (Beischer 1951).

Adsorption of the metallic stearates on platinum and mica is also purely physical, but nevertheless the stearates are more stable. This shows that desorption behaviour is influenced by the properties of the adsorbate in bulk as well as by adsorption forces. The stearate layers will have the same compositions and approximately the same packings as they had on the trough (100 per cent. calcium stearate or 70 per cent. copper stearate) and under the trough conditions used both would be the distearate (Sanders and Spink 1955). Copper distearate in bulk has a much higher softening temperature than stearic acid, and it is mainly this difference which accounts for the superior thermal stability of adsorbed stearate layers. The intrinsic stability of the stearates is apparently sufficient to overshadow any differences in thermal desorption behaviour between mica and platinum substrates. Finally, we note that in all these instances of purely physical adsorption the layers dissolve readily in benzene.

(*b*) *Chemical Reaction and Adsorption*

The results obtained with copper surfaces confirm that any pure acid initially present in the adsorbed layers soon reacts to form a soap. Thermal desorption was negligible in all experiments at a temperature where stearic acid would partially desorb from platinum and wholly from the basal plane of mica. This is in agreement with the work of Tanaka (1942), who observed stable electron-diffraction patterns from stearic acid layers on copper surfaces (*in vacuo*) up to 140 °C. The corresponding value for silver, which is unreactive to stearic acid, was only 60–70 °C. Strong adsorption of stearic acid on copper was also

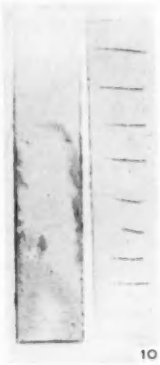
RADIOACTIVE TRACER STUDY OF ADSORBED LONG CHAIN MOLECULES

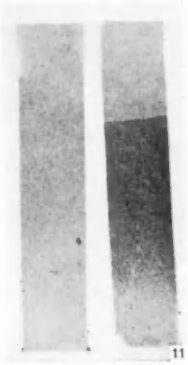


Typical autoradiographs.

Figs. 1 and 2.—Thermal desorption from mica surfaces.
Figs. 3 and 4.—Thermal desorption from platinum surfaces.
Fig. 5.—Thermal desorption from copper surfaces.
Fig. 6.—Dissolution by benzene of layers deposited on copper.

RADIOACTIVE TRACER STUDY OF ADSORBED LONG CHAIN MOLECULES





Typical autoradiographs.

Fig. 7.—Retracted layers of stearic acid on copper surfaces.
Fig. 8.—Typical artefact.
Fig. 9.—Vapour phase transport of stearic acid on mica.
Figs. 10, 11, and 12.—Vapour phase transport of copper stearate on mica, platinum, and copper surfaces respectively.

shown very clearly by Rideal and Tadayon (1954). The high softening temperature of stearates is, however, not the only reason for this very stable behaviour on copper, as benzene does not desorb stearate as readily from copper as from the other surfaces. It seems that some at least of the molecules in a layer adsorbed on copper are attached by forces which are essentially chemical. We may also conclude, from the experiments on desorption by benzene in general, that the action of this solvent on mixed layers of long chain compounds is to remove all molecules except those possessing such a bond.

These points may be discussed in the light of previous work on the interaction of stearic acid with copper surfaces. As noted in Section I, Bowden and Moore (1951) have shown that an excess of acid will react continuously and that part of the soap formed is removed by benzene. Similar results were obtained by Greenhill (1949), Daniel (1951), and Hirst and Lancaster (1951). With Langmuir-Blodgett or retracted layers, however, there is no possibility of continuous reaction and this restriction on the free acid supply is likely to modify the final state of the system. Other electron diffraction studies (e.g. Menter and Tabor 1951) have shown that surface soap formation takes place rapidly if an adsorbed layer of stearic acid on copper is heated above room temperature, and the same conclusion has been reached from experiments on lubrication (Gregory and Spink 1947). Reaction is thus possible on surfaces in the cold but becomes more marked if the stearic acid is to some extent thermally disordered or even melted. This increase in surface reaction at higher temperatures is also confirmed by the observation that layers deposited on copper have a greater resistance to solvent desorption if annealed first.

The actual mechanism of reaction is now considered to differ very little from the corresponding bulk process, where the soap is formed by an essentially ionic reaction with the metal oxide or hydroxide. An investigation by Tingle (1950) into the lubrication of freshly machined copper gave indirect evidence that oxidation must precede surface reaction, and also showed that the presence of water is necessary. The essential role of water was shown more directly in the work of Hirst and Lancaster, and confirmed by Lancaster and Rouse (1951) from calorimetric measurements. On the copper surfaces prepared by our techniques we should therefore expect reaction to take place rapidly, as both oxide and water were present and the cuprous oxide constituting the actual surface will be slightly permeable to copper ions (Tylecote 1950, review article). If the reaction were identical with the bulk process the product would be copper distearate, but owing to the limited supply of stearate radical it is probable that some monostearate will be present as well ; this will be true of layers deposited as acid or as part-stearate.

The mechanism of copper monostearate adsorption can be associated with the divalency of copper, and the consequent possibility that the second chemical bond links the stearate to the cuprous oxide substrate. This would be a much stronger bond than the purely physical dipole interaction by which the distearate and any unreacted pure acid would be adsorbed. It may be further postulated that the presence of an appreciable fraction of monostearate in a layer will make some contribution to the thermal stability of the whole.

Immersion of the deposited layers in benzene would then tend to remove the less strongly adsorbed distearate (and any unreacted acid), so that the density of the autoradiographs taken after this solvent treatment could be some indication of the amount of monostearate originally present. When *unlimited* stearic acid is available, however, as in the experiments of Bowden and Moore (1951), the distearate should predominate and its dissolution would account for the continuous reaction observed.

(c) *Influence of Water on Desorption*

The observation that physically adsorbed long chain molecules undergo thermal desorption more readily in a humid than a dry atmosphere is most interesting. The phenomenon is also noted by Rideal and Tadayon (loc. cit.) and is probably related to the effect which moisture has been shown to have on the lubrication of unreactive surfaces (Campbell 1940) and on spreading processes (Cotton 1947 ; Devaux 1947). It seems that water molecules may penetrate into adsorbed layers and enlarge the total area occupied or alternatively displace some of the original molecules. Campbell observed competing adsorption between water and fatty acid and found that whilst on reactive metals the acid could displace water, on glass the adsorbed water was not displaced. We may conclude that the physical adsorption of water is very similar to that of long chain fatty acids or soaps. Such a view is also supported by the measurements of Lancaster and Rouse (1951) who found the heats of adsorption, in the absence of reaction, to be the same for both water and fatty acid on metal oxide powders.

B. SURFACE TRANSPORT

I. Introduction

Molecules adsorbed on solid surfaces may, under certain conditions, migrate from one part of the surface to another. There is a clear distinction between this process and the spreading of comparatively large quantities of a liquid over a solid to form a thick, secondary, or duplex film. The surface migration of single molecules is governed by the forces operating between the surface and individual adsorbed molecules, rather than the interactions between the molecules themselves. True *surface diffusion* may be defined as the movement of molecules along a surface whilst remaining under the influence of an adsorption bond, and in some respects resembles solid state diffusion. There are, however, two other mechanisms which could bring the system to a similar final state. Complete desorption may occur, followed almost immediately by readsorption after some transport in the vapour phase. This will be referred to as the " vapour phase transport " mechanism. Alternatively, the adsorbed material may penetrate a very small distance into the lattice of the solid, and then move approximately parallel to the surface by a special form of volume diffusion. The surface regions of a solid, to a depth of a few atomic diameters, are known to have a very much greater volume diffusion coefficient than the normal value for the solid. Hence the major component of diffusion within this shallow zone will be parallel to the surface, and for such a process the term " diffusion in a surface region " may be proposed. It seems probable that all three mechanisms do actually exist,

though for any given system a particular one may predominate, and the others be inoperative.

A considerable amount of work has been published on the true surface diffusion process, most of which is concerned with systems where the distances moved by migrating molecules were very small and the methods of detecting this movement somewhat indirect. Typical examples are the classical experiments on the growth and erosion of crystals, carried out by Volmer and Adhikari (1925, 1926), and Volmer (1932), who inferred from their observations that even large molecules could be transported in this way. The movement of *small* molecules or atoms over greater distances ($\sim$1 mm) has been demonstrated in several studies of the behaviour of alkali or alkaline earth metals on tungsten at high temperatures (e.g. Langmuir and Taylor 1932 ; Becker and Moore 1940). Here the mechanism is described as " incipient evaporation " followed by lateral movement under the influence of a concentration gradient together with, in some instances, an electric field as well. A clear distinction was recognized between this and transport by processes involving complete evaporation and then recondensation, though at still higher temperatures some evidence of the latter was found.

Reports of surface transport over distances of $\sim$1 cm are few. Hardy (1922) concluded that the spreading of long chain organic compounds on solids proceeds in two stages, the first being a migration of one monomolecular layer only. This he considered to be definitely an example of vapour phase transport. Some positive evidence of surface transport is given in the paper by Beischer (1951) discussed in Part *A* of the present paper. Examination of partially coated mica specimens before and after annealing showed that the acid was not only retained at non-basal planes exposed by scratches, but had migrated on to scratches that were originally clean. On copper and lead surfaces migration was not observed. Rideal and Tadayon (1954) suggested that surface diffusion might play a part in the transfer of long chain material which they observed to take place between surfaces locally in contact. In addition, they gave details of a quantitative study in which measurements were made of the slow diminution in radiation from an island of active stearic acid monolayer on mica, the results being analysed assuming that this loss was wholly due to true surface diffusion. Finally, there are a number of reports of long range transport where the dominant mechanism is clearly diffusion in a surface region (e.g. Alty and Clark 1935 ; Nickerson and Parker 1950). This process, however, constitutes a separate field of investigation, and the possibility of its occurrence does not arise in the present work.

These experiments consist of a further application of radioactive tracer techniques to an elucidation of the long range surface migration process. By this means definite groups of adsorbed molecules were labelled, and observations made to ascertain the extent to which they might move over solid surfaces, and details of the mechanism operating. The actual systems used were designed to ensure, as far as possible, that the process observed would be true surface diffusion. Long chain molecules were used as diffusates and their behaviour studied on " clean " surfaces of silver single crystals, quartz glass, mica, and

polycrystalline platinum and copper. Thus there is no possibility of volume diffusion or diffusion within surface regions. Also, the low vapour pressure of the long chain compounds was expected to minimize vapour phase transport. The experimental techniques were similar to those described in Part *A*, with the addition of Geiger tube scanning as an alternative to autoradiography for detecting the tracer elements. It was found that true surface diffusion over macroscopic distances did not occur. The only change on increasing the temperature was a tendency for desorption, as described above, and by suitable control of the specimen ventilation this could be shown to lead to vapour phase transport over large distances.

II. Experimental Work

(*a*) *Techniques*

The first observations were made on layers of active material deposited by the Langmuir-Blodgett technique on cylindrical specimens of silver and quartz glass. Stepped layers were built up by immersing the cylinders, with their axes vertical, to varying depths on successive dips. This provides a form of surface concentration gradient at the start of each experiment, so that any observed redistribution of material after annealing would be an indication of some surface transport—either over the clean specimen itself or over an adsorbed layer of the long chain molecules. Cylindrical specimens were chosen because the diffusing system is then essentially one-dimensional, and the geometry is also convenient for scanning the surface with a Geiger tube.

The Geiger tube was specially designed for the purpose, and is illustrated in Figure 2, together with the arrangements for mounting and scanning the specimen. It is made from a solid block of brass by machining out the chambers and quench gas reservoirs. The anodes are mounted on glass to metal seals, and a rectangular aperture in the walls of one chamber forms the window as shown. A window covering of $3 \cdot 2$ mg/cm^2 aluminium foil was found satisfactory. The tube is used in conjunction with a β-emitting tracer in the diffusing compound, and, as the specimen can approach the window very closely, the resulting counts measure the quantity of material on a small and sharply defined part of the specimen. In a direction parallel to the specimen axis the resolution is *c.* $1 \cdot 5$ mm, which is probably about the minimum value consistent with reasonable counting times and the available specific activities in β-emitting compounds. A direct application of counting methods to surface transport investigations is thus limited to a search for comparatively long-range effects. The limit of resolution by autoradiography is of course much lower, but this technique cannot be made to yield useful quantitative results as readily as Geiger tube scanning. An improvement in the tube resolution could be obtained if the two chambers were operated in coincidence, but the corresponding reduction in sensitivity then becomes prohibitively great. The numerical results given below are, therefore, counts from the chamber *nearest* to the window operating alone.

The specimens were $11 \cdot 5$ mm in diameter and 40 mm long, with a prolongation of smaller diameter by which they could be mounted and accurately

centred on a supporting rod. Reproducible and constant counting geometry was further ensured by making the bearings for this rod in the form of spring-loaded V's. These allow both rotational and axial freedom, so that any part of the specimen surface can be brought before the window. The rotational movement was, however, very rarely used, as angular variations in counting rate were found to be negligible with freshly deposited layers, and check experiments showed that this was also true after annealing.

The annealing was carried out in the thermostat used for the desorption experiments, by removing the holder illustrated in Figure 1 and substituting the complete cylinder with its supporting assembly. Experiments were done at

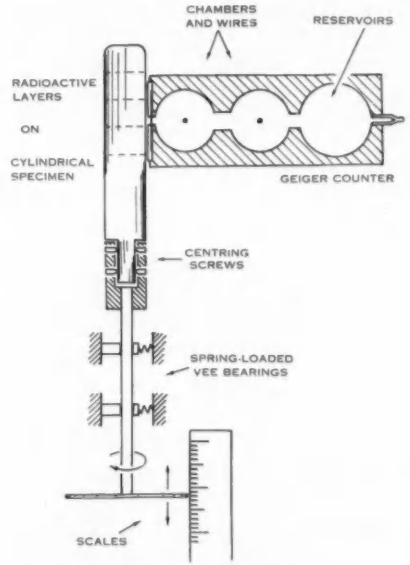


Fig. 2.—The Geiger counter and arrangement for scanning cylindrical specimens.

several different temperatures up to a maximum of 126 °C. Ventilation was again provided, using partially dried air which was passed over the surface in the direction of *increasing* surface concentration of deposited long chain material. This precaution was intended to suppress vapour phase transport effects, and the results show that it was quite successful.

Effects due to diffusion in cracks or grain boundaries were avoided by using single crystal or vitreous specimens. The silver specimen was made by casting with slow solidification from one end under high vacuum. Quartz glass specimens were formed from transparent quality tubing. Before immersion in the trough these specimens were cleaned to a reproducible condition. The silver, after a brief electropolish to remove contamination from the mould, was etched in a

1 : 3 hydrogen peroxide-ammonia mixture followed by a thorough rinsing in distilled water. In the electron diffraction camera the resulting surface gave a strong silver single crystal pattern with only very faint traces of contamination. The quartz glass specimens were cleaned in hot chromic acid and then distilled water.

The tracer element used was ^{35}S, as it was the only pure β-emitter which could be obtained at a sufficiently high specific activity for the scanning technique. The choice of a long chain molecule to contain the sulphur atom was restricted to those suitable for Langmuir-Blodgett deposition. Inactive compounds with various sulphur-containing groups were therefore prepared

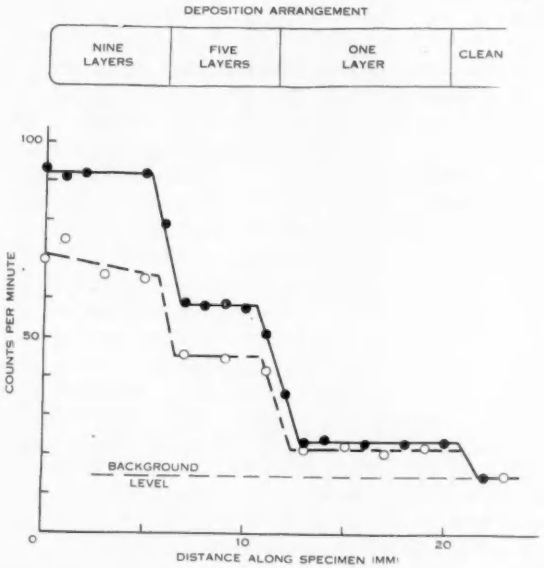


Fig. 3.—Distribution of activity from hydantoin layers on silver.
● as deposited ; ○ after annealing for 15 hr at 126 °C.

and tested for stable behaviour on the trough. The most favourable was α-mercaptostearic acid, $CH_3.(CH_2)_{15}.CH(SH).COOH$. With calcium or copper ions in the trough this compound deposited satisfactorily on both silver and quartz glass. From conductivity water the deposition was successful only on silver, possibly because on quartz glass the negative surface charge developed on immersion prevents adsorption of the pure acid.

(*b*) *Behaviour of Mercaptostearic Acid on Silver and Quartz Glass*

Preliminary experiments on surface diffusion were carried out with active mercaptostearic acid, synthesized from $Na^{35}SH$ supplied by the A.E.R.E. at a specific activity of 1·4 mc/mM. The steps on freshly deposited layers could

be resolved quite well, but no evidence of surface transport was detected after annealing. On silver the distribution of activity remained almost unchanged even after prolonged heating at *c.* 50 °C above the melting point of the mercapto acid, the only effect being a very slight loss of activity in layers deposited from conductivity water. Layers on quartz glass also showed some loss of activity at the same temperature. The counting rate was, however, too low for a reliable distinction to be made between purely negative results and the diffusion of small fractions of a monolayer.

A second series of experiments was, therefore, undertaken, using material of a higher activity which was prepared by a different synthesis. Labelled thiourea at 47 mc/mM was reacted with bromostearic acid to give the corresponding pseudothiohydantoin, some of which was then hydrolysed to the

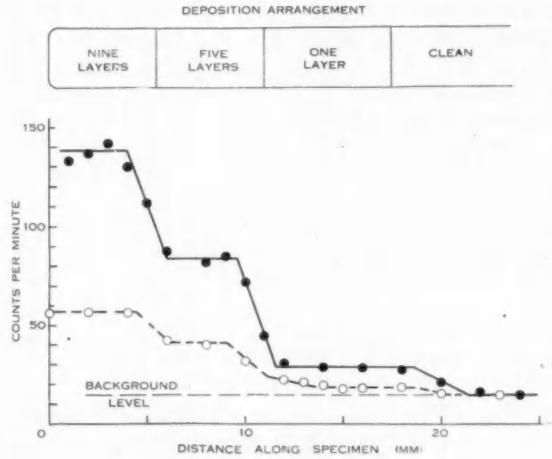


Fig. 4.—Distribution of activity from hydantoin layers on quartz.
● as deposited; ○ after annealing for 15 hr at 126 °C.

mercapto acid. The second stage was found to be accompanied by a considerable reduction in specific activity. Accordingly, the direct use of pseudothiohydantoin on the trough was tried and, with copper ions in solution, Langmuir-Blodgett layers could be deposited satisfactorily on both specimens. It is possible that hydrolysis occurs actually in the spread monolayer itself, and this would be followed, as in the case of the low-activity preparation, by a partial conversion to the corresponding copper soap.

A deposited monolayer derived from the hydantoin gave 10–14 counts/min above background. Typical results from experiments on silver and quartz glass are shown in Figures 3 and 4 respectively. In each graph the distribution of activity immediately after deposition is expressed by the lines ● and corresponds very closely to the nominal position of the "steps" as indicated. After annealing for 15 hr at 126 °C the specimens were rescanned and the lines ○

obtained. Again there is evidence only of desorption, with some difference in the behaviour of the two specimens. Quartz glass has lost nearly two-thirds of the activity from each step, including the single monolayer step, whilst on silver the desorption is less marked and the first monolayer remains almost complete.

It was also found that the activity of layers deposited on silver was not appreciably reduced by washing the specimen in benzene or light petroleum, especially if the layers had been annealed. These observations suggest that some chemisorption has occurred at the clean silver surface, even though the long chain compound is fairly stable. The behaviour of mercaptostearic acid adsorbed on to silver was therefore investigated further by electron diffraction experiments.

(c) Structural Changes in Adsorbed Mercaptostearic Acid when Heated

Langmuir-Blodgett layers of the acid were deposited, either from conductivity water or water containing calcium ions, on disks of polycrystalline silver cleaned as described above. These were then heated whilst under observation in the diffraction camera, using the technique of Menter and Sanders (1951), and patterns photographed at various temperatures up to and beyond the melting point of mercaptostearic acid, 79 °C. Freshly deposited layers were seen to be well orientated in all cases, the patterns from conductivity water deposition being characteristic of long chain acid and those from calcium solution indicating a mixture of acid and soap molecules. With increasing temperature the layers become disordered, the acid above 70 °C and the mixed acid-soap above 90 °C, and heating was continued further up to 90 and 120 °C respectively after which the specimens were immediately allowed to cool. Slow reorientation of the chains was later observed, showing that the compounds had not been desorbed or decomposed by a *brief* exposure to high temperatures.

The effect of prolonged heating was then studied, with layers of mercaptostearic acid formed both by Langmuir-Blodgett deposition and the evaporation of solution applied in bulk. For the deposited layers it was convenient to use the single crystal silver specimen, and after verifying that the layers gave typical orientated long chain patterns the specimen was annealed in the thermostat for 64 hours at *c.* 70 °C. When reexamined the areas originally covered by the layers then gave diffuse halo patterns, which could arise from disordered long chain material that had not yet reorientated, or alternatively had become unable to reorientate due to some reaction between the mercapto group and the silver surface. Definite evidence that a surface reaction of this type can occur was obtained from the experiments with thick films. Here a relatively gross quantity of the mercaptostearic acid was put on to a " clean " polycrystalline silver surface and the system annealed at 126 °C for some hours. The specimen was then washed in light petroleum, to remove any weakly adsorbed material, and examined in the camera. A strong ring pattern was obtained whose spacings indicated that the surface was covered with small crystals of silver sulphide, Ag_2S, together with some silver oxide. There were no traces of long chain material. It is therefore clear that when mercaptostearic acid is adsorbed

on silver the mercapto group can react with the metal, and at a sufficiently high temperature the molecule will break up and the long chain component desorb whilst most of the sulphur remains attached to the surface.

Such ease of reaction shows that ^{35}S is not a suitable tracer for surface transport studies on silver, and would be a sufficient reason for the negative results obtained. As, however, the observations on quartz glass were also negative, it seems that the failure to undergo true surface diffusion over macroscopic distances is an inherent property of the mercaptostearic acid molecule.

(*d*) *Investigation of Vapour Phase Transport*

The above results contrast with the observations of Beischer (1951), who found positive evidence for the surface transport of pure stearic acid over appreciable distances. As the ^{14}C tracer used for that work was an integral part of the long chain itself, there can be no doubt that the published autoradiographs represent movement of the whole molecule. This apparent distinction in behaviour between the pure and mercaptostearic acids could be due to the difference in molecular structure, but the experimental conditions suggest that the positive results were due to vapour phase transport. Similar experiments to those of Beischer were therefore carried out, using the materials and techniques of Part *A* but with a wider range of conditions during the diffusion anneal. Specimens were again prepared by depositing layers of ^{14}C-labelled stearic acid, or copper stearate, on to slips of mica, platinum, and copper. Autoradiographs were then made from these specimens before and after annealing them in the thermostat.

To obtain conditions unfavourable to vapour phase transport the slips were ventilated in the same way as the cylindrical specimens, using the special holder illustrated in Figure 1, with care taken to ensure ventilation *towards* the region of higher surface concentration of stearic acid. Experiments were done at various temperatures up to 150 °C and with wet and dry air. In no case was any surface transport observed, the behaviour of all the adsorbed layers being confined to progressive desorption as described in Part *A*, except that at temperatures above *c.* 120 °C there was some desorption even from copper surfaces.

Conditions especially favourable to vapour phase transport were then investigated. The technique consisted of mounting a prepared specimen and a clean specimen of the same material at various distances from each other in a glass tube, which was then sealed off and immersed in the thermostat. For this experiment the annealing atmosphere would be therefore only partially dry. After 1 hr at 91 °C the pair of specimens was removed and autoradiographed. Some transfer of long chain compound from the prepared to the clean specimen was found to have occurred in all cases, though the effect was most marked when the pairs were close together and desorption known to be easy. The extent of this vapour phase transfer for each combination of adsorbate and specimen material is noted in Table 1 (Part *A*) and typical autoradiographs of pairs are shown in Plate 2. These specimens had been annealed with small separations

of 1·5 mm. The process appears to be simply an approach to adsorption-desorption equilibrium over the whole area of the specimens and containing tube. It is most complete with the stearic acid and mica combination illustrated in Plate 2, Figure 9, all the sites for strong adsorption being filled and the remaining adsorbate evenly distributed over the basal planes.

A vapour phase mechanism can thus bring about appreciable surface transport of adsorbed molecules, even when their vapour pressure is quite low (e.g. ~0·02 mm Hg for stearic acid at 91 °C). However, a necessary condition is that the ambient atmosphere be restricted in volume, as the effect clearly becomes small if desorbed molecules can escape into an indefinitely large space. It would be reasonable to conclude, therefore, that the earlier reports of long range surface diffusion are probably examples of vapour phase transport.

It should be noted that insufficient care at one point in the experimental technique can lead to autoradiographs showing apparent surface diffusion on a large scale. If a " clean " specimen, wet from a final rinse, is partially immersed in the trough and the long chain compound spread and compressed *immediately*, the piston oil pressure will force the monolayer upwards on to the surface of the (thick) water film still present on the specimen. This gives rise to effects of the type illustrated by Plate 2, Figure 8, where a control specimen is shown to have active material on areas not intentionally immersed during deposition.

III. Discussion and Conclusions

In Part *A* it was concluded that long chain molecules adsorbed on to solid surfaces may readily desorb when thermally activated. We might therefore expect some appreciable surface diffusion to take place as well, but the experiments show clearly that such a phenomenon does not occur. This result may be compared with the evidence that *small* adsorbed molecules, or individual atoms, are capable of some surface diffusion without desorption (e.g. Langmuir and Taylor 1932; Lennard-Jones 1932; Lennard-Jones and Strachan 1935; and Becker and Moore 1940). A tentative explanation for the behaviour of our systems will be developed by considering the respective energy conditions involved in desorption and surface diffusion, and then the relative probabilities of a molecule taking part in each of these processes. Finally, the vapour phase transport mechanism will be discussed and some suggestions made for further work on the true surface diffusion process.

(*a*) *Desorption and Surface Diffusion*

The condition for desorption of a given molecule is the simultaneous breaking of all the bonds by which it is attached to the surface and its neighbours. With long chain compounds the total constraint includes the physical or chemical bonds due to the end groups and a small contribution from each $-CH_2-$group. Nevertheless, even with 15 or 16 (CH_2) groups in the chain, the constraint for a *physically* adsorbed molecule is evidently still small—not greatly different from that on a molecule in a bulk sample of the compound—as desorption occurs readily as soon as the temperature exceeds the bulk melting point. The essential

point for comparison with the diffusion process is that the energy condition has only to be satisfied once for the molecule to pass into the vapour phase and it is then likely to remain desorbed as (except for the special case of experiments carried out in a small enclosure) the concentration of long chain material is much lower in the vapour than the surface phase.

In the idealized model of true surface diffusion treated by Lennard-Jones (1932), a small and isolated molecule diffuses by movement from one position of minimum energy to an adjacent one. These positions have a periodicity which is associated with the crystal structure, and the energy increase between them constitutes the energy barrier for the process. However, this simple model is scarcely directly applicable to the case of long chain compounds, as here the molecule is large compared with the atomic surface periodicity and especially so when it is lying flat. Nevertheless the adsorption must still be " sited " to some extent. However, since in diffusion the surface bonds are not completely broken, the energy condition for diffusion must be less than that for desorption. This will be true of close packed as well as of isolated molecules.

A molecule will thus be activated to make a single diffusion movement very much more often than to desorb, but the resultant of these movements will not be resolvable unless they have a preferred direction. To satisfy this condition there must be some potential gradient acting on the molecule. In many surface diffusion systems a concentration gradient is the only one present, but when there are several types of adsorption site on the same surface—with different heats of adsorption—the resulting chemical potential gradient becomes important and molecules able to migrate will collect on the sites where this heat is greatest. Examples of migration under these circumstances have been studied in connection with crystal growth (Volmer 1932 ; Burton, Cabrera, and Frank 1951), and in the present work we have the instance of preferential adsorption provided by mica with its basal and non-basal planes.

However, in the present systems both the concentration and the chemical potential gradients are in the form of " steps ", so that the lateral force on the adsorbed molecules will tend to be confined to those in the immediate vicinity of these steps, and to be negligible for those in the relatively large areas between. This restriction on the numbers of molecules which can participate in diffusion has no parallel in the desorption process, as the effective concentration gradient normal to the surface is everywhere large, though even so there is evidence that desorption is more marked at such monolayer steps (Karle 1949). Hence we must conclude that probability favours desorption and the maximum movement anywhere of a molecule by true surface diffusion, before being desorbed is below the limit of resolution of the observational techniques used. No theoretical estimates of this distance have yet been made for large molecules, though the reality of their surface migration by successive short movements has been shown directly in one special case (Müller 1950 ; Gomer and Speer 1953). We may, however, note that the distance suggested by de Boer (1953) for small adsorbed molecules or atoms, in equilibrium with their vapour, is also of a very low order of magnitude ($\sim$1 μ assuming a very favourable preferred direction for all unit movements).

(*b*) *Vapour Phase Transport*

When specimens are annealed in the thermostat an equilibrium between the adsorbed long chain material and its vapour is not possible, and any molecules which desorb are lost to the system. Such an equilibrium may be attained in a small closed vessel, and under the conditions of extreme mobility which molecules possess whilst in the vapour phase it is evident that both the concentration and the chemical potential gradients can bring about marked redistribution of the adsorbates. The process is also very rapid, except in systems where chemisorption is operating.

The extent to which the vapour phase mechanism can account for other published reports of surface migration would depend on the control over the ambient atmosphere. Where experiments are carried out within a definite enclosure, as in the classical work on " primary spreading " by Hardy (1922), or in the transfer process observed by Rideal and Tadayon (1954), there can be no doubt that an evaporation-condensation process of this type is operative. If there is no intentional control, then the observation of transport could be an indication of some vapour phase diffusion through the stationary " boundary layer " of permanent gases (e.g. Volmer and Adhikari 1926). An intermediate stage is exemplified by the work of Beischer (1951), who observed transport over distances of several mm on specimens annealed under conditions which probably involved an almost closed containing vessel. It is interesting to note that these authors used large adsorbed molecules and refer to the possibility of evaporation but the implications are not considered in detail. The experiments on surface diffusion described by Rideal and Tadayon may also be interpreted as evaporation, and the similarity between their quoted activation energies for diffusion and for transfer suggests that both are, in fact, the energy for desorption.

As a system for studying vapour phase transport, the physically adsorbed long chain molecule is therefore very suitable, and its movements may be conveniently followed by the use of radioactive tracers. For the detection and study of true surface diffusion, however, a different experimental approach is required. In order that probability should favour migration, a system must be chosen in which the diffusing molecule has a large heat of adsorption which varies only slightly from point to point on the surface. There must be a large lateral force tending to produce migration, for example, a steep chemical potential gradient as well as a concentration gradient. Lastly, the method of detecting movement should have a resolution considerably better than 1 μ if the phenomenon is to be observed quantitatively. At present this is not possible by radioactive tracer techniques.

IV. Acknowledgments

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THE MECHANISM OF THE ALKALI CATALYSED PHENOL–FORMALDEHYDE REACTION

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Summary

Kinetic studies on the 2,3,4,5-tetramethylphenol(prehnitenol)- and 2,6-xylenol-formaldehyde reactions indicate that the alkali catalysed reaction is not a simple bimolecular reaction. The rate of the 2,6-xylenol-formaldehyde reaction in the presence of excess alkali has been shown to be proportional to

$$[\text{phenoxide}]^{1.4} \quad [\text{formaldehyde}]^{1.4} \quad [\text{free alkali}]^{-0.4}.$$

The mechanism of the reaction has been interpreted as a reaction between the phenoxide ion and $CH_2{=}O$ together with other simultaneous reactions. It is unlikely that the ion CH_2OH^+ plays any part in the alkali catalysed reaction. Attempts have been made to interpret the results on the basis that a hemiformal rearranges to a phenol alcohol and that the ion CH_2OPh^+ reacts with a phenoxide ion. In any case it is not possible to give a complete mechanism with certainty. The degree of formation of hemiformal is too small to be detected by hydrogen ion measurements.

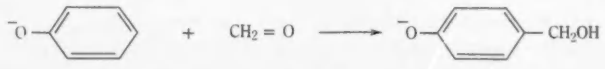
When the Cannizzaro reaction of formaldehyde is carried out in the presence of a phenol, the phenoxide ions catalyse a condensation which is presumably an aldol condensation. This reaction having a long induction period and being autocatalytic does not assume importance in the early stages of the reaction.

A compound, probably 2,2′-dihydroxy-3,3′,4,4′,5,5′,6,6′-octamethyldiphenylmethane, has been isolated from the alkaline reaction between prehnitenol and formaldehyde.

I. INTRODUCTION

The phenol-formaldehyde reaction is of importance in the very extensive synthetic resin industry, and in the past much effort has been spent studying the various phases in the formation of phenol-formaldehyde resins (Carswell 1947 ; Ziegler 1948 ; Finn, Megson, and Whittaker 1950 ; Hultzsch 1950, 1951 ; Zinke 1951 ; Walker 1953). The interpretation of the results has been difficult, because of the high reactivity of the compounds used and the large number of compounds formed during the reaction.

Some attempts have been made to study the kinetics of the initial stages of the phenol-formaldehyde reaction, which in alkaline solution, leads to the formation of *ortho-* or *para-* phenol alcohols.



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The results of these investigations are in the main very confusing, some workers finding either first or second order reactions with slight changes in conditions. The following division of the more important papers is therefore not clear cut.

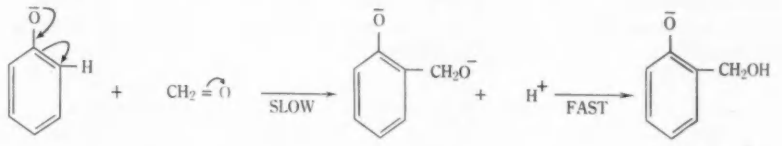
First order reactions have been reported for various phenols by Sprung (1941), Jones (1946, 1950), and Raff and Silverman (1951*a*, 1951*b*). However, Goldblum (1950) claimed that Jones's results indicated a second order reaction.

Second order reactions for a number of phenols have been found by Euler and Kispéczy (1941), Stults (1949), Debing, Murray, and Schatz (1952), Stults, Moulton, and McCarthy (1952), de Jong and de Jonge (1953), and Freeman and Lewis (1954).

Stults (1949) found, however, that the second order constants increased with pH and passed through a maximum at about pH 9·5. Debing, Murray, and Schatz (1952) also found that the second order constants increased with the alkali concentration.

On the other hand, de Jong and de Jonge (1953) showed that the rate varied linearly with the hydroxyl concentration but with alkali equivalent to or greater than the phenol concentration the rate was independent of the alkali concentration.

The mechanism of the alkali catalysed phenol-formaldehyde reaction has been discussed by Pepper (1941), Dewar (1949), and de Jong and de Jonge (1953), who suggest that it is a reaction between the phenoxide ion and $CH_2{=}O$, such as



Ingram (1951) in his discussion of the reaction between resorcinol and formaldehyde suggests that the resorcinolate ion reacts with both $CH_2{=}O$ and $\overset{+}{C}H_2OH$.

Apart from the work of de Jong and de Jonge (1953) no attempt has been made to differentiate between the relative reactivities of the phenoxide ion and the undissociated phenol, and thus determine whether the catalytic effect of the alkali is entirely due to the formation of the more highly reactive phenoxide ion. However, the results of de Jong and de Jonge (1953) differ from those of Stults (1949), Debing, Murray, and Schatz (1952), and those obtained in the present investigation.

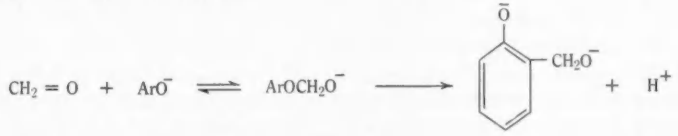
The work now describes an attempt to elucidate the mechanism of the reaction between formaldehyde and certain phenols in dilute alkaline solution using kinetic data from accurate measurements. To restrict the reaction to the formation of the phenol monoalcohol, the monoreactive phenols, 2,6-xylenol and 2,3,4,5-tetramethylphenol (prehnitenol), were used. An excess of alkali was used to render the phenol soluble in water and to convert it all to the phenoxide ion, even though this introduced a complication because the Can-

nizzaro reaction of formaldehyde occurred simultaneously with the phenol-formaldehyde reaction. An alternative would be to use a mixed solvent, but objections are that alcohols would form acetals with the formaldehyde, and ketones would be condensed by alkali. A very attractive solvent appeared to be dioxane-water, but unfortunately, the rate of the Cannizzaro reaction increases rapidly with increasing dioxane content (Pajunen 1950).

The work will be discussed in sections dealing with the possibility of using hydrogen ion measurements to determine the extent to which a phenol and formaldehyde may combine as a hemiformal, the effect of a phenol on the rate of the Cannizzaro reaction, and the rates of the reaction of formaldehyde with 2,3,4,5-tetramethyl- and 2,6-dimethylphenol.

II. Hemiformal Formation

One mechanism (Walker 1953), which has been suggested to explain the phenol-formaldehyde reaction, is that a hemiformal is formed initially which rearranges to a phenol alcohol



If a hemiformal is formed in any appreciable concentration from the phenol and formaldehyde then there will be changes in the hydroxyl ion concentration which will be indicated by hydrogen ion measurements. This is evident from a consideration of the following equilibria:

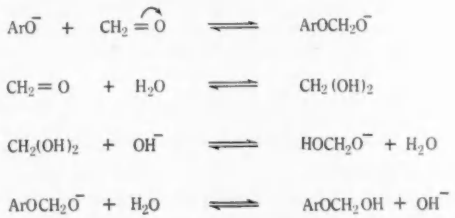


Table 1 gives the experimentally determined hydroxyl ion concentrations of alkaline solutions of formaldehyde with and without sodium mesitoxide. An examination of the results shows that the addition of sodium mesitoxide causes no change in the hydroxyl ion concentration.

It can be argued however that the total alkali concentrations are not the same in both cases, but the following calculations will show that the hydroxyl ion concentration is governed only by equilibria (**1**) and (**2**) which do not involve any hemiformal.

$$CH_2(OH)_2 + OH^- \overset{K_1}{\rightleftharpoons} HOCH_2O^- + H_2O, \quad \ldots\ldots\ldots \quad (1)$$

$$ArOH + OH^- \overset{K_2}{\rightleftharpoons} ArO^- + H_2O. \quad \ldots\ldots\ldots\ldots \quad (2)$$

Now if a is the excess NaOH after neutralizing the mesitol, b the total formaldehyde, c total phenol, and K_1, K_2 the hydrolysis constants of formaldehyde and mesitol respectively, then

$$[HOCH_2O^-]+[OH^-]+[ArO^-]=a+c,$$
$$[CH_2(OH)_2]+[HOCH_2O^-]=b,$$
$$[ArO^-]+[ArOH]=c,$$

it follows that:

$$[OH^-]^3+[OH^-]^2\{K_1+K_2-a+b\}+[OH^-]\{K_2(K_1-a-c+b)-K_1a\}-K_1K_2(a+c)=0, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

$$[CH_2(OH)_2]=\frac{K_1b}{K_1+[OH^-]}, \quad \ldots\ldots\ldots\ldots\ldots (4)$$

$$[ArO^-]=\frac{c[OH^-]}{\{K_2+[OH^-]\}}. \quad \ldots\ldots\ldots\ldots\ldots (5)$$

The value for K_1 is 0·134 (Martin 1954*a*) and for K_2 is 0·00085.* Although the dissociation constant of formaldehyde, as determined by the electrometric method, is regarded as an approximate figure (Martin 1954*a*) it is advisable for strict comparison to use this value here.

TABLE 1

HYDROXYL ION CONCENTRATION IN THE SYSTEM MESITOL-NaOH-CH_2O IN WATER AT 40 °C

NaOH (g-mol l^{-1})	CH_2O (g-mol l^{-1})	Na Mesitoxide (g-mol l^{-1})	OH^- (g-mol l^{-1})	
			Expt.	Calc.
0·02644	0·04806	—	0·0205	—
,,	,,	—	0·0198	—
,,	,,	—	0·0202	—
,,	,,	—	0·0197	—
0·02538	,,	0·02728	0·0200	0·0201
0·02564	,,	0·02702	0·0197	0·0203

The various values of a, b, c, K_1, and K_2 were substituted in equation (3) and the actual hydroxyl ion concentration was calculated by the method of successive approximation. The calculated values for the hydroxyl ion concentration are given in Table 1 and agree with the experimental values. It follows that the amount of hemiformal present, if any, is so small that the actual hydroxyl ion concentration is governed only by the above equilibria.

III. KINETIC EXPERIMENTS

Rates of reaction were calculated from the changes in concentration of formaldehyde, and in some instances of alkali also, measured after dilute solutions of formaldehyde and the phenol had been heated in the presence of excess sodium

* The dissociation constant of mesitol and 2,6-xylenol was determined at 40 °C with the cell, Ag | AgCl(s) | NaCl, 2,6-xylenol or mesitol, NaOH | H_2(g) | Pt black, in an apparatus similar to that described by Hamer and Acree (1939) and Bates and Acree (1943). The values obtained were $0·45\times10^{-10}$ g-mol l^{-1} for 2,6-xylenol and $0·32\times10^{-10}$ g-mol l^{-1} for mesitol at an ionic strength of $\mu=0·4$.

hydroxide. Aliquots of the test solution were heated in sealed tubes in a thermostat for known periods. Details of the experimental methods are given in Section V. Since the changes in alkali concentration are very small compared with the large total amount of alkali present, this determination was less accurate than the measurements of the changes in formaldehyde concentration, and where one only is essential for the calculations, the formaldehyde figure alone is used.

No simple treatment of the results of the kinetic experiments has been found possible. Their interpretation will be discussed by making a series of assumptions as to the mechanism, showing where the simpler ones are inadequate, and building on these to obtain a closer correlation with the data. For an adequate explanation it was found essential to distinguish between the different ionic or molecular forms of formaldehyde present, and to calculate their concentration.

(*a*) *Effect of 2,4,6-Trimethylphenol (Mesitol) on the Cannizzaro Reaction*

Since there is an excess of alkali over that required to neutralize the phenol there will be a simultaneous Cannizzaro reaction of formaldehyde leading to the formation of methanol and formic acid

$$2CH_2{=}O + OH^- \rightarrow HCOO^- + CH_3OH.$$

It was quickly found that this simultaneous Cannizzaro reaction was occurring and complicated the study of the phenol-formaldehyde reaction, and that the first need was to find the effect upon the rate of the Cannizzaro reaction of a phenol such as 2,4,6-trimethylphenol (mesitol) which would not participate in a phenol-formaldehyde reaction under mild conditions.

With certain limitations the Cannizzaro reaction of formaldehyde may be described as second order with respect to total formaldehyde and first order with respect to alkali (Martin 1954*b*). The rate is therefore given by

$$\frac{dy}{dt} = k_3(a - y/2)(b - y)^2,$$

so that

$$k_3 = \frac{2}{t(2a-b)}\left[\frac{1}{b-y} - \frac{1}{b} - \frac{2\cdot303}{2a-b}\log_{10}\frac{b(a-y/2)}{a(b-y)}\right],$$

where a is the initial alkali concentration or the excess alkali after neutralizing the phenol, b the initial concentration of formaldehyde, and y the change in formaldehyde concentration at time t.

The results of two kinetic runs with and without the addition of mesitol, and for which k_3 has been calculated, are given in Table 2. For the experiment without mesitol it will be noticed that 78 per cent. of the formaldehyde has reacted and throughout the run a consistent set of third order velocity constants has been calculated.

On the other hand, for the run containing the mesitol, a consistent set of third order velocity constants has been calculated up to about 60 per cent. reaction of the formaldehyde. At this stage the values calculated for k_3 began to increase rapidly and at the same time the formaldehyde concentration was rapidly reduced to almost zero. This is shown in Figure 1. This effect was also

accompanied by the appearance of a yellow colour in the solution which became deeper as the reaction proceeded. Pajunen (1950) noticed the formation of a

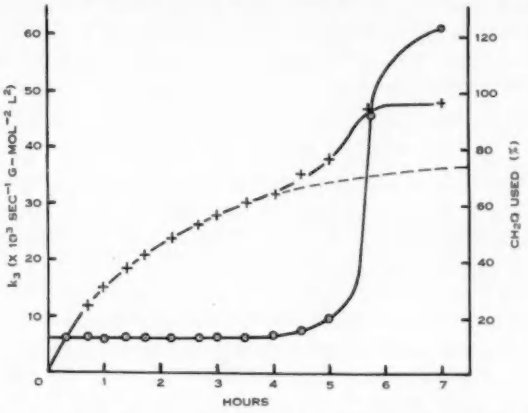


Fig. 1.—The influence of mesitol on the Cannizzaro reaction of formaldehyde. ⊙ $k_3 \times 10^3$ sec^{-1} g—mol^{-2} l^2. + Percentage CH_2O used.

yellow colour in some of his experiments on the Cannizzaro reaction and explained that it was due to an aldol condensation. From the results given in Table 2

TABLE 2

THIRD ORDER VELOCITY CONSTANTS FOR THE CANNIZZARO REACTION OF FORMALDHYDE IN 10 PER CENT. DIOXANE-WATER AT 60°C

CH_2O (0·0914M) NaOH (0·2178N) Na Mesitoxide (0·1018N)			CH_2O (0·0751M) NaOH (0·3143N) Na Mesitoxide (absent)		
Time (hr)	CH_2O Used (%)	$k_3 \times 10^3$ (sec^{-1} g-mol^{-2} l^2)	Time (hr)	CH_2O Used (%)	$k_3 \times 10^3$ (sec^{-1} g-mol^{-2} l^2)
0·33	13	6·41	0·33	14	5·93
0·72	24	6·41	0·67	24	5·78
1·00	30	6·04	1·00	33	5·82
1·38	37	6·16	1·50	45	6·57
1·72	42	6·25	2·00	50	5·96
2·17	48	6·20	2·50	55	5·96
2·67	53	6·21	3·00	59	5·98
3·00	56	6·53	3·50	63	5·96
3·50	60	6·46	4·00	67	6·13
4·00	64	6·68	4·75	70	6·04
4·50	70	7·88	5·50	73	6·10
5·00	76	9·79	6·50	76	6·15
5·75	94	46·0	7·50	78	6·05
7·00	96	61·5			

it is concluded that the reaction has a long induction period, is autocatalytic, and that the phenoxide ions catalyse the reaction.

This effect appears likely to be general for all phenols because we have observed a similar sudden reduction of the formaldehyde concentration in the exploratory work on the prehnitenol-formaldehyde reaction. This made it possible to study the phenol-formaldehyde reaction only over the initial stages, and even so care was needed to ensure that the aldol condensation did not interfere.

(*b*) *Reaction between 2,3,4,5-Tetramethylphenol (Prehnitenol) and Formaldehyde*

Our study of a phenol-formaldehyde reaction was commenced with 2,3,4,5-tetramethylphenol (prehnitenol) because it can only be monoreactive at its one free *o*-position. It was also thought that without altering the mechanism of the reaction the two *m*-methyl groups by hyperconjugation with the *o*-position would increase the rate as compared with 2,4-xylenol.

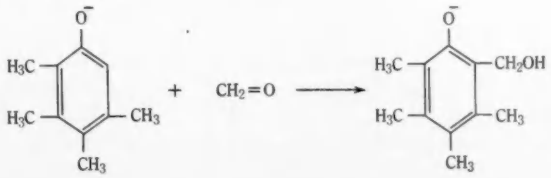
Since the reaction between phenol and formaldehyde is an aromatic substitution, the phenoxide ion will have a greater reactivity than the phenol because of the much increased electron accession to the *o*- and *p*-positions. This electron accession is the sum of the inductive and electromeric effects:

For the inductive effect the O^- group repels electrons while the OH group attracts electrons and therefore the hydroxyl group will tend to deactivate the ring. In the case of the electromeric effect the O^- group releases electrons much more readily than the OH group. Therefore the overall effect of the electron displacements is to give the phenoxide ion a greater reactivity than the phenol. Since among the concentration of reactants that of phenol is very small, only the phenoxide ion concentration need be considered in this discussion.

Formaldehyde reacts as $CH_2{=}O$ through the electron processes

but the concentration of $CH_2{=}O$ is small and proportional to the total formaldehyde which exists largely as methyleneglycol in aqueous solution.

The prehnitenol-formaldehyde reaction in the presence of alkali will involve the initial formation of a phenol alcohol.



It is reasonable to assume that the reaction is second order between the phenoxide ion and formaldehyde. The calculations show, however, that this is not the case and that the rate varies inversely as some function of the hydroxyl ion concentration.

At first sight it would appear that the electrophilic reagent required for the aromatic substitution is the ion $\overset{+}{C}H_2OH$, for the formaldehyde exists in aqueous solution as methyleneglycol and can ionize in the following way

$$CH_2(OH)_2 \rightleftharpoons \overset{+}{C}H_2OH + OH^-.$$

The concentration of CH_2OH will be small and proportional to $[CH_2(OH)_2]/[OH^-]$. However, Wadano, Trogus, and Hess (1934) have found that the pK value of the ionization involved is 20 and at the dilutions used in the present investigation, the concentration of $\overset{+}{C}H_2OH$ would be 10^{-18} g-mol l^{-1} or smaller. In all probability the concentration of $\overset{+}{C}H_2OH$ is too small for it to take a detectable part in the reaction. In confirmation of this, Martin (1954*b*) has shown that $\overset{+}{C}H_2OH$ does not participate in the Cannizzaro reaction of formaldehyde.

An alternative explanation, which leads to the same rate equation for the phenol-formaldehyde reaction as derived for the ion $\overset{+}{C}H_2OH$, is that the hemiformal $ArOCH_2OH$ rearranges to a phenol alcohol by a first order reaction.

TABLE 3

PREHNITENOL-FORMALDEHYDE REACTION IN 10 PER CENT. DIOXANE WATER AT 60 °C

Original concn.: 0·1030N prehnitenol; 0·1046N CH_2O; total 0·2193N NaOH. $w = 0{\cdot}267$*
Concn. at $t = 0$: 0·0972N CH_2O; total 0·2171N NaOH

Time (hr)	0·25	0·75	1·00	1·25	1·50	2·00	2·50	3·00	3·55	4·00
x ml 0·03992N†‡	0·35	0·87	1·08	1·22	1·43	1·67	1·84	2·02	2·16	2·26
y „ „ †‡	1·19	3·10	3·82	4·46	5·04	6·01	6·87	7·51	8·13	8·60
Cannizzaro reaction (%)	59	56	57	55	57	56	54	54	53	53
Assumption No. 1										
$k_3 \times 10^3$ sec^{-1} g-mol^{-2} l^2	5·25	5·43	5·42	5·44	5·52	5·62	5·86	5·95	6·12	6·33
$k_2 \times 10^4$ sec^{-1} g-mol^{-1} l	4·88	4·72	4·57	4·45	4·38	4·24	4·18	4·05	3·94	3·90
Assumption No. 2										
$k_1 \times 10^5$ sec^{-1}	5·49	5·22	5·03	4·88	4·77	4·56	4·45	4·27	4·13	4·06

* $w = x/y$.

† x and y are expressed in ml of 0·03992N solution per 5·60 ml aliquots.

‡ x, change in NaOH concn.; y, change in formaldehyde concn.

In the calculations given below the validity of two mechanisms for the phenol-formaldehyde reaction will therefore be tested: (i) it is a bimolecular reaction, and (ii) it results from a unimolecular rearrangement of a hemiformal. The results of three prehnitenol-formaldehyde runs are given in Tables 3, 4, and 5. The change in alkali concentration x is a measure of the Cannizzaro reaction and is associated with a change $2x$ in the formaldehyde concentration. The change in formaldehyde concentration y is a measure of the total Cannizzaro and phenol-formaldehyde reactions.

TABLE 4

PREHNITENOL-FORMALDEHYDE REACTION IN 10 PER CENT. DIOXANE WATER AT 60 °C

Original concn.: 0·1000N prehnitenol; 0·1077M CH_2O; total 0·3209N NaOH. $w=0·406$*

Concn. at $t=0$: 0·0983M CH_2O; total 0·3159N NaOH

Time (hr)	0·20	0·40	0·60	0·80	1·00	1·33	1·67	2·00	2·33	2·67	3·00
x ml 0·04053N†‡	0·51	1·03	1·41	1·74	1·98	2·40	2·66	2·94	3·09	3·26	3·38
y „ „ †‡	1·33	2·35	3·36	4·08	4·83	5·76	6·56	7·23	7·81	8·17	8·67
Cannizzaro reaction (%)	77	88	84	85	82	83	81	81	79	80	78
Assumption No. 1											
$k_3\times10^3$ sec^{-1} g-mol^{-2} l^2	5·81	5·68	6·00	5·92	6·13	6·20	6·33	6·48	6·65	6·52	6·82
$k_2\times10^4$ sec^{-1} g-mol^{-1} l	2·76	2·56	2·58	2·44	2·42	2·30	2·22	2·14	2·08	1·96	1·54
Assumption No. 2											
$k_1\times10^5$ sec^{-1}	5·80	5·34	5·32	5·00	4·92	4·65	4·44	4·26	4·12	3·87	3·80

* $w=x/y$.

† x and y are expressed in ml 0·04053N solution per 5·60 ml aliquots.

‡ x, change in NaOH concn.; y, change in formaldehyde concn.

TABLE 5

PREHNITENOL-FORMALDEHYDE REACTION IN 10 PER CENT. DIOXANE WATER AT 60 °C

Original concn.: 0·1008N prehnitenol; 0·1077M CH_2O; total 0·1450N NaOH. $w=0·125$*

Concn. at $t=0$: 0·0989M CH_2O; total 0·1442N NaOH

Time (hr)	0·25	0·50	0·75	1·00	1·25	1·50	1·75	2·00	2·50	3·00	3·50	4·25
x ml 0·04022N†‡	0·14	0·25	0·36	0·45	0·51	0·62	0·67	0·74	0·90	0·98	1·10	1·22
y „ „ †‡	1·18	2·04	3·08	3·77	4·11	4·68	5·18	5·65	6·35	6·79	7·30	7·95
z „ „ †‡	—	—	—	—	—	—	0·18	0·44	0·58	1·25	1·59	1·84
Cannizzaro reaction (%)	24	25	23	24	25	27	26	26	28	29	30	31
Assumption No. 1												
$k_3\times10^3$ sec^{-1} g-mol^{-2} l^2	6·36	5·82	6·60	6·50	5·90	5·99	6·08					
Assumption No. 2												
$k_1\times10^5$ sec^{-1}	3·47	3·20	3·47	3·36	3·02	2·99	2·95					

* $w=x/y$.

† x, y, and z are expressed in ml of 0·04022N solution per 5·54 ml aliquots and represent changes in NaOH, CH_2O, and diphenylolmethane concn., respectively.

‡ x, change in NaOH concn.; y, change in formaldehyde concn.; z, change in diphenylolmethane concn.

The Cannizzaro reaction within a run is accurately described by a third order law (Martin 1954*b*) so that its rate is given by

$$\frac{d(2x)}{dt}=k_3(b-y)^2(a-c'-x), \quad \ldots\ldots\ldots\ldots (6)$$

where a is the total NaOH concentration at zero time, b is the formaldehyde concentration at zero time, and c' is the original concentration of prehnitenol. If it is assumed that the dissociation constants of the phenol and phenol alcohol are approximately the same (Sprengling and Lewis 1953) then the amount of alkali required to neutralize the total phenol and phenol alcohol will be c', the original concentration of phenol. The concentration of the phenol at zero

time was calculated, when necessary, from the weight initially added and the changes in formaldehyde and alkali concentrations during the heating-up period.

(i) *Assumption No. 1 : Bimolecular Reaction.*—If the reaction between the formaldehyde and the phenoxide ion is assumed to be bimolecular, the rate will be given by

$$\frac{\mathrm{d}(y-2x)}{\mathrm{d}t}=k_2(b-y)(c-y+2x), \quad \ldots\ldots\ldots\ldots \quad (7)$$

where c is the concentration of prehnitenol at zero time.

To solve the differential equations (6) and (7) accurately involves some difficult integrations which were circumvented by using a simple relationship between x and y. If x is plotted against y (Fig. 2), a straight line is obtained for those runs given in Tables 3 and 4. This is not general as is shown by the results plotted in Figure 3, although there is a linear relationship between x and y for the initial stages of the reaction. Therefore, for those runs given in Tables 3 and 4, $x=wy$ where w is a coefficient which can be evaluated by the method of least squares. It follows that the percentage Cannizzaro reaction is $200x/y=200w$ and the constancy of this value throughout a run is illustrated in Tables 3 and 4.

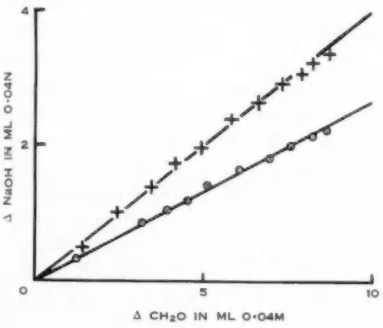


Fig. 2.

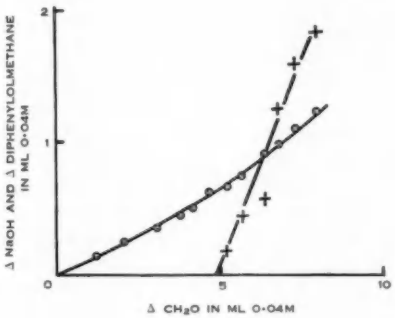


Fig. 3.

Fig. 2.—Variation of change in alkali concentration with total change in formaldehyde concentration. ⊙ From Table 3. + From Table 4.

Fig. 3.—The variation of the changes in the alkali and diphenylolmethane concentrations with changes in formaldhyde concentrations. ⊙ Δ NaOH. + Diphenylolmethane.

By substituting $x=wy$ in equations (6) and (7) it is a simple matter to integrate both so that the integrated forms are

$$k_3t=\frac{2w}{a-c'-wb}\left[\frac{1}{b-y}-\frac{1}{b}-\frac{w}{a-c'-wb}\ln\frac{b(a-c'-wy)}{(a-c')(b-y)}\right],$$

and

$$k_2t=\frac{1-2w}{c-b(1-2w)}\ln\frac{b[c-y(1-2w)]}{c(b-y)}.$$

The values calculated for k_3 and k_2 are given in Tables 3 and 4 under Assumption No. 1. It will be noticed that a good set of third order velocity constants is obtained over the initial stages of the reaction and then as the reaction proceeds these values begin to increase. These third order velocity constants are of the same magnitude as those determined independently at the same alkali and formaldehyde concentrations, as shown in Table 6.

TABLE 6

THIRD ORDER VELOCITY CONSTANTS FOR THE CANNIZZARO REACTION OF FORMALDEHYDE IN 10 PER CENT. DIOXANE-WATER AT 60 °C

Formaldehyde (M)	NaOH (N)	$k_3 \times 10^3$ (sec^{-1} g-mol^{-2} l^2)
0·0873	0·1024	4·90
0·0724	0·2053	5·64
0·0751	0·3143	6·01

On the other hand, the values calculated for k_2 for the prehnitenol-formaldehyde reaction decrease with time. From a comparison of the values for k_2 for the two runs Tables 3 and 4, it will be observed that k_2 is approximately halved on doubling the alkali concentration and, therefore, a further assumption is necessary to account for this.

(ii) *Assumption No. 2 : Hemiformal Reaction.*—To account for the observed inverse effect of the hydroxyl ion concentration it is assumed that the hemiformal is formed and rearranges to a phenol alcohol by a first order reaction. It has already been shown that the hemiformal, if formed, is in too small concentration to be detected by hydrogen ion measurements, but its reactivity could be sufficient for it to take part in the reaction. The concentration of the hemiformal is proportional to $[ArO^-][CH_2(OH)_2]/[OH^-]$ and the rate of the prehnitenol-formaldehyde reaction now becomes

$$\frac{d(y-2x)}{dt} = k_1 \frac{[CH_2(OH)_2][ArO^-]}{[OH^-]}$$

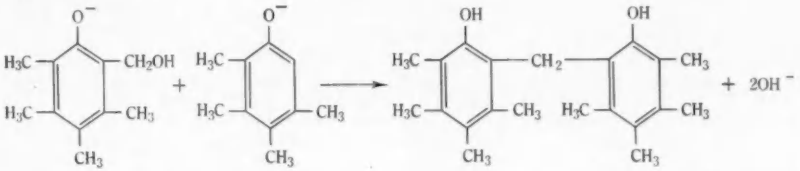
$$= k_1 \frac{(b-y)(c-y+2x)}{a-c'-x},$$

putting $x = wy$ and integrating

$$k_1 t = \frac{1-2w}{c-b(1-2w)}\left[(a-c'-wb)\ln\frac{b}{b-y} - \frac{(a-c')(1-2w)-wc}{1-2w}\ln\frac{c}{c-y(1-2w)}\right].$$

The values calculated for k_1 are given in Tables 3 and 4 (under Assumption No. 2) and it will be noticed that these values decrease with time, but nevertheless are the same magnitude for both runs. This assumption, though it does not explain the results completely, leads to a closer approximation than Assumption No. 1.

(iii) *Formation of Diphenylolmethane.*—It was found that a diphenylolmethane, 2,2′ - dihydroxy - 3,3′,4,4′,5,5′,6,6′ - octamethyldiphenylmethane precipitated as the free acid from the hot solution during the reaction. The quantity of this formed during a run is given in Table 5 (as z) and plotted in Figure 3.



The diphenylolmethane would be formed from the reaction between a phenol and a phenol alcohol molecule, and would interfere because the hydroxyl ion concentration would be greater than expected and the phenoxide ion concentration less than expected during a run.

Since a short period elapses before the diphenylolmethane is formed then it would be interesting to examine the rate constants for the initial stages of the reaction where the hydroxyl ion concentration would be accurately known. An examination of the values for k_3 (the Cannizzaro constants) in Tables 3, 4, and 5 for Assumption No. 1 indicate that they are constant over the initial stages and then begin to increase as expected. On the other hand, the values of k_1 and k_2 calculated for the prehnitenol-formaldehyde reaction for Assumptions 1 and 2 still vary with time during the initial stages of the reaction.

TABLE 7

INITIAL RATES FOR THE PREHNITENOL-FORMALDEHYDE REACTION IN 10 PER CENT. DIOXANE-WATER AT 60 °C

Run Number	1	2	3
NaOH (g-mol l^{-1})	0·1163	0·2209	0·0442
CH_2O (g-mol l^{-1})	0·1046	0·1077	0·1077
Prehnitenol (g-mol l^{-1})	0·1030	0·1000	0·1008
P-F* rate $\times 10^5$ (g-mol l^{-1} sec^{-1})	0·45	0·20	1·06
Cannizzaro rate $\times 10^5$ (g-mol l^{-1} sec^{-1})	0·72	1·52	0·25
P-F rate $\times$ [NaOH] $\times 10^6$ (g-mol^2 l^{-2} sec^{-1})	0·52	0·44	0·47

* P-F, prehnitenol-formaldehyde.

It is obvious from this discussion that the prehnitenol-formaldehyde reaction is complex and that it is difficult to calculate the constants during a run, because of the uncertain correction to be applied for the hydroxyl ion concentration. The results indicate that the reaction is certainly not bimolecular and that the rate is inversely proportional to some function of the hydroxyl ion concentration. If the rate is inversely proportional to the hydroxyl ion concentration then the product of the initial rate and the hydroxyl ion concentration should be a constant for the same concentrations of prehnitenol and formaldehyde. That this is not the case is shown from the results in Table 7.

(c) *2,6-Xylenol-Formaldehyde Reaction*

The reaction between 2,6-xylenol and formaldehyde is free from the complication of an insoluble product and because of greater solubility it is not necessary to include dioxane in the solvent. The results of three runs are given in Tables 8, 9, and 10, with the values for k_1 and k_3 calculated on the basis of

TABLE 8

2,6-XYLENOL-FORMALDEHYDE REACTION IN WATER AT 60 °C

Original concn. : 0·1110N 2,6-xylenol ; 0·0979M CH_2O ; total 0·3414N NaOH. w=0·295. Concn. at t=0 : 0·1089N 2,6-xylenol ; 0·0929M CH_2O ; total 0·3398N NaOH

Rate Constants	Time (min)							
	6·0	12·0	18·0	24·0	30·0	36·0	42·0	48·0
$k_3 \times 10^3$ sec^{-1} g-mol^{-2} l^2	4·87	5·08	4·95	4·97	4·99	5·10	4·85	4·93
$k_1 \times 10^4$ sec^{-1}	1·48	1·49	1·42	1·40	1·37	1·36	1·28	1·27

TABLE 9

2,6-XYLENOL-FORMALDEHYDE REACTION IN WATER AT 60 °C

Original concn. : 0·2197N 2,6-xylenol ; 0·0981M CH_2O ; total 0·4534N NaOH. w=0·161. Concn. at t=0 : 0·2128N 2,6-xylenol ; 0·0879M CH_2O ; total 0·4522N NaOH

Rate Constants	Time (min)								
	3·0	6·0	9·0	12·0	15·0	18·0	22·0	26·0	30·0
$k_3 \times 10^3$ sec^{-1} g-mol^{-2} l^2 ..	5·95	5·28	5·26	4·76	4·84	5·17	5·25	5·14	5·21
$k_1 \times 10^4$ sec^{-1}	2·83	2·43	2·36	2·12	2·11	2·19	2·16	2·07	2·05

TABLE 10

2,6-XYLENOL-FORMALDEHYDE REACTION IN WATER AT 60 °C

Original concn. : 0·1084N 2,6-xylenol ; 0·1357N CH_2O ; total 0·3387N NaOH. w=0·296. Concn. at t=0 : 0·1059N 2,6-xylenol ; 0·1295M CH_2O ; total 0·3373N NaOH

Rate Constants	Time (min)							
	9·0	15·0	18·0	21·0	24·0	27·0	30·0	33·0
$k_3 \times 10^3$ sec^{-1} g-mol^{-2} l^2	4·08	4·07	4·14	4·02	4·17	4·21	4·24	4·21
$k_1 \times 10^4$ sec^{-1}	1·84	1·76	1·75	1·72	1·71	1·69	1·69	1·65

Assumption No. 2 of the preceding section, namely, that the xylenol-formaldehyde rate is proportional to the xylenol and formaldehyde concentrations and inversely proportional to the hydroxyl ion concentration.

The values calculated for k_1 for the xylenol-formaldehyde reaction show variations both within and between runs. On doubling the xylenol concentra-

tion, Tables 8 and 9, k_1 is almost doubled, so apparently the rate is proportional to the square of the xylenol concentration. There is no change in the percentage Cannizzaro reaction on increasing the formaldehyde concentration (Tables 8 and 10) as is shown by identical values of w. Since the Cannizzaro reaction is proportional to the square of the formaldehyde concentration a similar relationship would be expected for the xylenol-formaldehyde reaction. However, this is not strictly correct because the Cannizzaro velocity constant decreases with increasing initial formaldehyde concentration. Since the first order constant for the xylenol-formaldehyde reaction increases with the formaldehyde concentration, it would then appear that the rate is proportional to the formaldehyde concentration raised to a power between one and two.

(i) *Study of Initial Rates.*—Thus, on the basis of a simple assumption with regard to the rate of the xylenol-formaldehyde reaction, it has not been possible to calculate a satisfactory series of constants and it has been concluded that this method of treating the results is inadequate for the complex reaction. The method was altered and initial rates were determined and correlated with the change in concentration of one of the reactants, the concentrations of the others remaining constant. These results are given in Table 11.

The actual concentrations of OH^-, $CH_2(OH)_2$, and ArO^- are also given in Table 11, having been calculated from equations (**3**), (**4**), and (**5**), which are based on the equilibria shown in equations (**1**) and (**2**). The hydrolysis constant of formaldehyde K_1 is taken as $0{\cdot}30$ g-mol l^{-1} which is derived from the kinetic data on the Cannizzaro reaction (Martin 1954*b*) and is a more appropriate figure to use than the one from electrometric measurements. The hydrolysis constant K_2 for 2,6-xylenol is $6{\cdot}0\times10^{-4}$ g-mol l^{-1} which is calculated from the dissociation constant $0{\cdot}45\times10^{-10}$ g-mol l^{-1} at 40 °C.*

From these concentrations of hydroxyl ions and methyleneglycol the rates of the Cannizzaro reaction in each run may be calculated, for it has been shown previously (Martin 1954*b*) that this reaction is the sum of a third and fourth order reaction

$$\text{rate}=k_3[CH_2(OH)_2]^2[OH^-]+k_4[CH_2(OH)_2]^2[OH^-]^2.$$

The constants for these have the values $3{\cdot}35\times10^{-4}$ sec^{-1} g-mol^{-2} l^2 and $9{\cdot}02\times10^{-3}$ sec^{-1} g-mol^{-3} l^3 respectively. The xylenol-formaldehyde rate may then be obtained by difference, and the values are given in Table 11.

An examination of these xylenol-formaldehyde rates indicates the following approximate relationships: For a fourfold increase in phenoxide ion concentration the rate increases 6–8 times, runs Nos. 1–9 and Nos. 11–14. For a threefold increase in the total formaldehyde concentration the rate increases five times, runs Nos. 11 and 17 and Nos. 5–7, 15, and 16. For a fourfold increase in the total alkali concentration the rate is reduced to half or a third of its former value, runs Nos. 1–3 and 14 and Nos. 5–7, 12 and 13. That is, the rate is proportional to [phenoxide]$^{1{\cdot}2\text{ to }1{\cdot}5}$ [formaldehyde]$^{1{\cdot}4}$ [alkali]$^{-0{\cdot}4}$.

* See footnote, p. 197.

TABLE 11

2,6-XYLENOL-FORMALDEHYDE RATES IN WATER AT 40 °C

Run No.	Ionic Strength	Free NaOH (g-mol l^{-1})	Total CH_2O (g-mol l^{-1})	2,6-Xylenol (g-mol l^{-1})	$[OH^-]$ (g-mol l^{-1})	$[CH_2(OH)_2]$ (g-mol l^{-1})	$[ArO^-]$ (g-mol l^{-1})	Total Rate $\times 10^6$ (sec^{-1} g-mol l^{-1})	C.R.* Rate $\times 10^6$ (calc.) (sec^{-1} g-mol l^{-1})	P-F† Rate $\times 10^6$ (sec^{-1} g-mol l^{-1})	P-F Rate $\times 10^4$ $[ArO^-][CH_2(OH)_2]$ (sec^{-1} g-mol^{-1} l)	$\frac{[ArO^-]}{[OH^-]^2}$ (g-mol^{-1} l)	P-F Rate $\times 10^6$ (calc.) (sec^{-1} g-mol l^{-1})
1	0·4089	0·2071	0·1012	0·2018	0·1712	0·0644	0·2011	4·93	1·34	3·59	2·77	6·86	2·96
2	0·4089	0·2072	0·1012	0·2017	0·1712	0·0644	0·2010	4·86	1·34	3·52	2·72	6·86	2·96
3	0·4034	0·2013	0·0982	0·2005	0·1669	0·0631	0·1998	4·51	1·22	3·29	2·61	7·17	2·89
4	0·4042	0·2012	0·0973	0·1995	0·1672	0·0625	0·1988	4·06	0·98	3·08	2·48	7·11	2·85
5	0·3025	0·2005	0·0992	0·1004	0·1659	0·0639	0·0954	2·53	1·24	1·29	2·12	3·47	1·35
6	0·3025	0·2007	0·0987	0·1003	0·1659	0·0636	0·0999	2·44	1·23	1·21	1·91	3·63	1·41
7	0·4026	0·2010	0·0991	0·1002	0·1661	0·0638	0·0998	2·57	1·24	1·33	2·09	3·62	1·41
8	0·4056	0·2055	0·1012	0·0504	0·1692	0·0647	0·0502	1·96	1·32	0·64	1·97	1·75	0·71
9	0·2524	0·2017	0·0989	0·0501	0·1666	0·0636	0·0499	1·73	1·24	0·49	1·54	1·80	0·69
10	0·2021	0·0998	0·0983	0·0996	0·0796	0·0777	0·0989	2·60	0·51	2·09	2·72	15·61	1·91
11	0·4014	0·0519	0·1011	0·0504	0·0406	0·0892	0·0497	1·22	0·23	0·99	2·23	30·15	1·25
12	0·1512	0·0495	0·0980	0·0991	0·0392	0·0867	0·0976	3·24	0·20	3·04	3·59	63·52	3·03
13	0·4016	0·0503	0·0995	0·1000	0·0406	0·0876	0·0985	3·70	0·25	3·45	4·00	59·78	3·02
14	0·4056	0·0542	0·1012	0·2017	0·0440	0·0883	0·1990	7·79	0·25	7·54	4·29	102·8	7·86
15	0·3028	0·2010	0·1980	0·1000	0·1385	0·1355	0·0996	7·48	4·03	3·45	2·56	5·19	3·03
16	0·3025	0·1996	0·2949	0·0991	0·1172	0·2120	0·0986	11·89	7·34	4·55	2·18	7·17	4·80
17	0·4014	0·0519	0·3020	0·0504	0·0276	0·2766	0·0493	5·76	1·23	4·53	3·32	64·7	4·91

* C.R., Cannizzaro reaction.

† P-F, xylenol-formaldehyde reaction.

However, the concentrations of hydroxyl ion and methyleneglycol are interdependent and the above relationship does not apply to these entities. A threefold increase in the total formaldehyde concentration, for example, gives a threefold increase in the methyleneglycol concentration, but this is accompanied by a reduction in the hydroxyl ion concentration.

The inverse effect of the hydroxyl ion concentration is analogous to that expected from Assumption No. 2, that the hemiformal rearranges by a first order reaction to a phenol alcohol, but the index of $[OH^-]$ in the expression is not unity. However, the difficulty can be removed if the rate is the result of two independent simultaneous reactions and is given by

$$\text{rate} = k_4[ArO^-][CH_2(OH)_2] + k_5\frac{[ArO^-][CH_2(OH)_2]}{[OH^-]}.$$

Qualitatively, this expression accounts for the variation of the rate with the methyleneglycol and hydroxyl ion concentrations, but it is linear with respect to the phenoxide ion concentration. If this equation accurately described the rate, the function,

$$\text{rate}/[ArO^-][CH_2(OH)_2],$$

should be a linear function of the reciprocal of the hydroxyl ion concentration. Figure 4, the graph of this relation, shows that this is not so; far less do the points fall on a line parallel to the abscissa as would be required for a simple second order reaction.

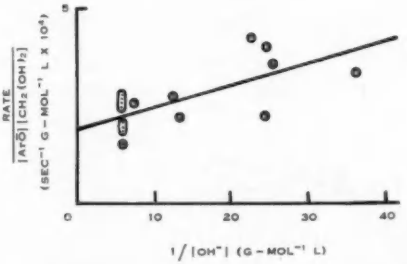
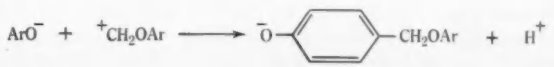


Fig. 4.—Variation of $\frac{\text{rate}}{[ArO^-]\,[CH_2(OH_2]}$ with $\frac{1}{[OH^-]}$.

It is possible that the phenoxy group could stabilize the formation of the ion $\overset{+}{C}H_2OAr$ by a powerful inductive effect $\overset{\delta+}{C}H_2 \leftarrow \overset{\delta-}{O}Ar$, and this ion could react with the phenoxide ion to give the ether



However, this ether has never been isolated from a phenol-formaldehyde reaction, in fact, this class of aromatic ethers has not been reported. If formed they should be stable to alkali and are unlikely to hydrolyse to the phenol alcohol.

If the interaction of hemiformal ion and phenoxide ion has only a minor role in the phenol-formaldehyde reaction, such products might escape detection.

If now the reaction of ArO^- with both $CH_2{=}O$ and $\overset{+}{C}H_2OAr$ is considered, the following equilibria are involved

$$ArO^- + CH_2(OH)_2 \rightleftharpoons ArOCH_2OH + OH^-,$$

and

$$ArOCH_2OH \rightleftharpoons \overset{+}{C}H_2OAr + OH^-.$$

From these it follows that the concentration of $\overset{+}{C}H_2OAr$ is proportional to $[ArO^-][CH_2(OH)_2]/[OH^-]^2$, and equation (**8**) is obtained as the expression for the rate, namely,

$$\text{rate} = k_4[ArO^-][CH_2(OH)_2] + k_5\frac{[ArO^-]^2[CH_2(OH)_2]}{[OH^-]^2}. \quad \ldots\ldots (8)$$

This is a quadratic function of the phenoxide ion concentration and, therefore, qualitatively accounts for the rate being proportional to $[ArO^-]^{1\cdot4}$.

For equation (**8**), rate/$[ArO^-][CH_2(OH)_2]$ should be a linear function of $[ArO^-]/[OH^-]^2$ and the results plotted in Figure 5 approximate to a straight line. The coefficients k_4 and k_5 were evaluated by the method of least squares

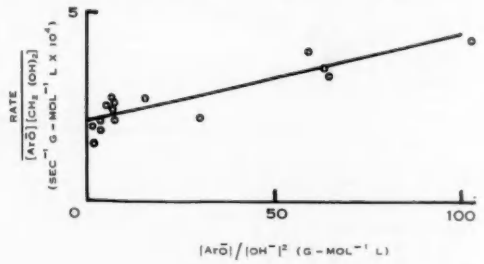


Fig. 5.—Variation of $\dfrac{\text{rate}}{[ArO^-][CH_2(OH)_2]}$ with $\dfrac{[ArO]}{[OH^-]^2}$.

and with these values the rate of the xylenol-formaldehyde reaction was calculated. As shown in Table 11 a rough agreement is found with the experimental values.

To sum up, the phenol-formaldehyde reaction is very complex and possibly consists of a reaction between the phenoxide ion and $CH_2{=}O$ together with

other reactions. It seems unlikely that the ion $\overset{+}{C}H_2OH$ participates in the alkali catalysed reaction. The experimental results cannot be explained by the rearrangement of the hemiformal to a phenol alcohol.

A rough agreement with experiment is obtained if it is assumed that the phenoxide ion reacts with $CH_2{=}O$ and with $\overset{+}{C}H_2OAr$. However, the experimental evidence is insufficient to assign any mechanism to the reaction with certainty. The results obtained in this investigation agree with those of Stults (1949) and Debing, Murray, and Schatz (1952) that the reaction is complex and is not simply bimolecular as indicated by de Jong and de Jonge (1953).

IV. Comments on Some Previous Work

Stults (1949) studied the reaction of sodium *p*-phenol sulphonate with formaldehyde and obtained a bimolecular reaction within a run at a constant pH. However, the bimolecular constant varied with the pH and passed through a maximum at about a pH of 9·4. This can be partly explained by the fact that with an increasing hydroxyl ion concentration the more reactive phenoxide ion is formed and the rate will therefore increase until nearly all the phenol is converted to phenoxide ion. At this stage the free hydroxyl ion concentration will increase and the inverse effect of the hydroxyl ion will operate and the rate will begin to decrease. On this basis the maximum observed by Stults agrees with the observations made in this investigation.

Table 12

PHENOL-FORMALDEHYDE VELOCITY CONSTANTS IN WATER AT 80 °C

Results of Debing, Murray, and Schatz (1952)

$k \times 10^6$ (sec^{-1} g-mol^{-1} kg)	NaOH (g-mol kg^{-1})
9·6	0·025
15·0	0·0375
19·4	0·050
50·0	0·100

Debing, Murray, and Schatz (1952) studied the reaction of phenol with formaldehyde at very low alkali concentrations. These workers were able to calculate an extremely good set of bimolecular constants within a run, provided certain values were assigned to the relative reactivities of the *o*- and *p*-positions in phenol and its substitution products. Such a procedure is very risky and it would be possible to adjust any set of calculated velocity constants which tended to vary with time. In any case the rate at zero time will be given accurately by the product of the velocity constant and the concentrations of the reactants.

Since the concentrations of phenol and formaldehyde are constant the rate is proportional to the velocity constant. Since the concentration of hydroxyl ions in the system is very small it is not necessary to correct for the formaldehyde

anion. At the low alkali concentrations used by Debing, Murray, and Schatz it is justifiable to assume that the phenoxide ion concentration is equal to the concentration of added alkali. If it is assumed that the phenoxide ion has a much greater reactivity than the phenol then, for a bimolecular reaction between the formaldehyde and phenoxide ion, the velocity constant should vary linearly with the added alkali concentration. An examination of the results given in Table 12 shows that the velocity constant increases at a greater rate than corresponds with linearity and, therefore, it appears that the rate is proportional to a power of the phenoxide ion concentration greater than one. These results are not incompatible with the findings of this investigation.

V. Experimental

(*a*) *Preparation and Purification of Materials.*—Carbonate-free NaOH was prepared by filtering 50% NaOH rapidly through a sintered glass funnel, and diluting with CO_2-free water. The NaOH solution was adjusted to 1·0N and stored in " Polythene " or wax-coated bottles.

The formaldehyde solution was prepared by heating paraformaldehyde under reflux with water until it had passed into solution, and the solution was filtered, analysed, and diluted to 1·0N.

The dioxane was purified by the method described by Weissberger and Proskauer (1935). The dioxane was always freshly distilled from sodium just before use and tested for peroxides with KI.

The prehnitenol was prepared by the fusion of sodium prehnitene sulphonate with alkali as described by Töhl (1888). The prehnitenol was purified by fractional distillation at atmospheric pressure and the distillate crystallized once from 80–100 °C light petroleum, in order to obtain the prehnitenol in a form which could be easily handled.

The 2,6-xylenol was supplied by Messrs. L. Light & Co. Ltd., Wraysbury, England. It was purified by fractional distillation and then crystallized from 80–100 °C light petroleum.

The mesitol was prepared from *p*-cresol by the method of Barclay, Burawoy, and Thomson (1944) and Burawoy (1946). It was purified by fractional distillation at atmospheric pressure and then crystallized from 80–100 °C light petroleum.

The product *2,2′-dihydroxy-3,3′,4,4′,5,5′,6′,6-octamethyldiphenylmethane* was prepared under conditions similar to those in which it was obtained during kinetic experiments. A solution of prehnitenol (1·5 g in 100 ml, c. 0·10N), NaOH (0·14N), and formaldehyde (0·10N) was sealed in a glass tube and placed in a thermostat at 60 °C for 4 hr. A solid began to crystallize from solution after approx. 1½ hr. The solid was filtered on a sintered glass filter, pressed hard, and dried in a desiccator over calcined K_2CO_3. Yield 0·34 g.

To show that the compound had separated as the free phenol, diphenylolmethane (0·1 g) was weighed in an Erlenmeyer flask, shaken with aqueous ethanol, and titrated with H_2SO_4, using bromocresol purple as indicator. The amount of NaOH present corresponded to a concentration 1/34 of that required to form the monosodium salt of the diphenylolmethane. This NaOH would be that present in the adhering mother liquor and the compound therefore precipitates as the free acid. The NaOH was removed by washing with water and ethanol, and the purified compound then dried. It melted at 225–227 °C (Found : C, 80·9 ; H, 9·0 ; O, 10·2%. Calc. for $C_{21}H_{28}O_2$: C, 80·8 ; H, 9·0 ; O, 10·3%).

(*b*) *Kinetic Procedure.*—The phenols were weighed in a standard flask which had been swept out with CO_2-free argon and in those cases where the solution was 10% dioxane-water, 10 ml of dioxane was added by pipette. An aliquot of NaOH was then added and when the phenols had dissolved, was followed by an aliquot of formaldehyde and the necessary amount of 1·000N KNO_3 to maintain the ionic strength of the final solution at $\mu = 0·4$. The solution was diluted to 100 ml with CO_2-free water, and 5–7 ml aliquots of this solution were placed in constricted " Monax " tubes, sealed under argon, and placed in the thermostat. After allowing 10 min for tubes and thermostat to reach the required temperature, the first of the tubes was removed, and the time

measured from this instant. The reaction was stopped by immersing the tubes in a freezing mixture of equal volumes of carbon tetrachloride and chloroform mixed with crushed solid carbon dioxide. For analysis each tube was crushed under water in a thick walled glass vessel.

The thermostat was maintained constant to within 0·02 °C.

(c) *Analytical Methods.*—The NaOH concentration was determined by titration with dilute H_2SO_4, using bromocresol purple as the indicator. The total NaOH is defined as that which can be directly titrated with acid and includes that alkali required to form a Na phenate but not that forming Na formate. The free NaOH is defined as the excess remaining after the phenol has been completely neutralized.

The formaldehyde was determined by a modified Romijn's cyanide method (Walker 1953, p. 388) in which strongly acidified $AgNO_3$ solution containing 4 ml conc. HNO_3/g $AgNO_3$ was added to the almost neutralized reaction product between formaldehyde and cyanide. The solution was filtered and excess $AgNO_3$ titrated potentiometrically with ammonium thiocyanate. The amount of alkali originally present and the amount formed from the cyanohydrin reaction was approximately known, and an amount of H_2SO_4 equivalent to this was added to neutralize the CH_2O-KCN reaction mixture. A high acidity was essential because the AgCN must be precipitated in acid solution to avoid large discrepancies. In Romijn's original method the CH_2O-KCN reaction mixture was added to the acid $AgNO_3$. The procedure was altered in order to reduce the number of operations by allowing precipitation of the whole sample in the vessel in which the tube was crushed.

It was found that a small amount of reaction took place during the neutralization and it was therefore necessary to determine the alkali and formaldehyde on separate tubes.

For the determination of the diphenylolmethane the frozen tube was first thawed out and then opened with a hot spill of glass. The contents of the tube were washed out and filtered through a sintered glass crucible. The precipitate was washed with water, dried over $CaCl_2$, and weighed. The diphenylolmethane was removed from the crucible by washing with acetone and then water and the crucible again dried and weighed. The quantity of diphenylolmethane was given by the difference in the two weighings. This procedure was necessary in order to prevent errors from splinters of glass.

The solubility of the diphenylolmethane was determined by shaking weighed quantities for 17 hr at 60 °C with aqueous dioxane containing alkali approximately equal to that used in the run and then freezing the tube. The undissolved diphenylmethane was determined as above. The solubility in 10% dioxane-water was found to be 0·37 g/l.

The amount of the diphenylolmethane weighed was corrected for solubility in the alkaline solution.

(d) *Calculations.*—For determining the initial rate of the xylenol- and prehnitenol-formaldehyde reactions the total change in formaldehyde concentration y, was related to time t, by the empirical relationship $y=t/(m+nt)$, where m and n are coefficients which were evaluated from the linear relation $t/y=m+nt$, by the method of least squares. The rate at any particular time t was obtained by differentiation and is given by $dy/dt=m/(m+nt)^2$. In the calculations the rate was extrapolated to the concentration of formaldehyde of the solution as originally prepared.

The hydrogen ion measurements were made with the cell

$$\text{Hg} \mid \text{HgCl(s)} \mid \text{NaCl} \left| \begin{matrix} \text{NaCl, NaOH} \\ \text{CH}_2\text{O, mesitol} \end{matrix} \right| \text{H}_2\text{(g)} \mid \text{Pt black}$$

and were carried out in the manner described by Martin (1954*a*).

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STUDIES ON MAGNESIUM AND CALCIUM OXYCHLORIDES

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Summary

The reactions which take place in the system MgO-$MgCl_2$-H_2O at concentrations of $MgCl_2$ solutions up to 45 per cent. and temperatures from 0 to 110 °C have been studied in detail. Four oxychlorides have been found, namely, $9Mg(OH)_2.MgCl_2.5H_2O$, $5Mg(OH)_2.MgCl_2.8H_2O$, $3Mg(OH)_2.MgCl_2.8H_2O$, and $2Mg(OH)_2.MgCl_2.4H_2O$; and an equilibrium diagram has been produced which gives the conditions at which each is stable. It is probable that in the formation of the oxychlorides a complex ion forms first and this reacts with $Mg(OH)_2$, formed by rapid hydration of MgO, to produce amorphous oxychloride gels which slowly crystallize.

The reactions in the systems MgO-$CaCl_2$-H_2O, CaO-$MgCl_2$-H_2O, $Ca(OH)_2$-$MgCl_2$-H_2O, CaO-$CaCl_2$-H_2O, $Ca(OH)_2$-$CaCl_2$-H_2O, and between calcined dolomite and $MgCl_2$, or $CaCl_2$, solutions have been studied briefly. Oxychlorides form in these reactions also. It is therefore suggested that the explanation for the success of the method of Demediuk (1952) for the removal of " unsoundness " of dolomitic limes, and other limes high in magnesium oxide, by the action of salt solutions lies in the conversion of free magnesium oxide to magnesium oxychlorides.

The optical properties and stabilities of the magnesium oxychlorides are briefly discussed.

I. INTRODUCTION

An important industrial problem arising from the use of limes high in magnesium oxide is the slow hydration of the magnesium component which can produce extensive damage to masonry structures (Wells, Clarke, and Levin 1948, 1952). In the past it has been common practice in the United States of America to autoclave these limes so as to complete the hydration of the magnesium oxide before use, but recently Demediuk (1952) has evolved a simple method for correcting the " unsoundness " by treating the limes with magnesium or calcium chloride solutions. It was deduced that this treatment converts free magnesium oxide into magnesium oxychlorides, but the mechanism of the reactions was not clear nor were the compositions known of the oxychlorides so formed. Consequently, a study was undertaken of the chemistry of the basic reactions involved in oxychloride formation and of the identity and properties of the compounds formed. The present paper deals largely with the chemistry of oxychloride formation; a separate paper (Cole and Demediuk 1955) describes the identity, structure, and stabilities of magnesium oxychlorides and their high temperature derivatives.

Reactions between magnesium oxide and magnesium chloride and calcium oxide and calcium chloride have been the subject of many early investigations

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(Sorel 1867; Davis 1872; André 1882; Robinson and Waggaman 1909; Maeda 1926; Maeda and Yamane 1928; Feitknecht 1926, 1927, 1930; Lukens 1932; Bury and Davies 1932; Chassevent 1934), but it is only in recent years (Feitknecht and Held 1944; Walter-Lévy and de Wolff 1949; de Wolff and Walter-Lévy 1949, 1953; Walter-Lévy and Bianco 1951) that the composition of the compounds formed has been established with certainty. Products formed by reaction in water between magnesium oxide and chloride are frequently gel-like and tend to retain free magnesium oxide and chloride. It is consequently difficult to be certain of the composition of a reaction product without examining it by X-ray diffraction or differential thermal analysis methods. These techniques in their present state of development were naturally not available to the early workers.

Prior to 1932 magnesium oxychlorides were expressed by the general formula $x\text{MgO}.\text{MgCl}_2.y\text{H}_2\text{O}$ in which x varied from 1 to 10 and y from 10 to 21. However, the later work of Lukens (1932), Bury and Davies (1932), and Chassevent (1934) shows that two compounds with characteristic X-ray diffraction powder photographs exist with x equal to 3 and 5. The number of water molecules for the 3-form was given as 11, whereas that for the 5-form was unknown; the latter occurred at intermediate stages in the reactions. Chassevent, whose work has formed the starting point for the more recent investigations, introduced an important technique (followed in this investigation) of pressing samples instead of washing to remove excess magnesium chloride.

Feitknecht and Held (1944) confirm the existence of these two magnesium oxychlorides and express their compositions as $3\text{Mg(OH)}_2.\text{MgCl}_2.7\text{H}_2\text{O}$ and $5\text{Mg(OH)}_2.\text{MgCl}_2.7\text{H}_2\text{O}$. They also show, by X-ray examination, that another oxychloride with a molecular ratio of Mg(OH)_2:MgCl_2 equal to 4 is a mixture of the 3- and 5-forms. Later studies by Walter-Lévy and de Wolff (1949) and de Wolff and Walter-Lévy (1949, 1953) have shown that both the 3-form and the 5-form have 8 molecules of water and that the 3-form is always preceded in its formation by the 5-form. They also show that in the presence of carbon dioxide and water both compounds are converted into the basic chlorocarbonate $\text{Mg(OH)}_2.2\text{MgCO}_3.\text{MgCl}_2.6\text{H}_2\text{O}$. Finally, Walter-Lévy and Bianco (1951) report the existence of two other oxychlorides, $2\text{Mg(OH)}_2.\text{MgCl}_2.4\text{H}_2\text{O}$ and $9\text{Mg(OH)}_2.\text{MgCl}_2.5\text{H}_2\text{O}$ formed in solutions at, or above, a temperature of 100 °C.

In the present paper the system $\text{MgO-MgCl}_2\text{-H}_2\text{O}$ is reexamined at temperatures between 0 and 110 °C. Although no new crystalline oxychlorides have been discovered, the results present a much more systematic picture of the transformations within the systems than has yet been published. The reaction processes involved in oxychloride formation have been studied by examining, during the course of the reactions, the composition of the products by chemical, X-ray, and differential thermal analysis (D.T.A.) methods, and the temperature rise and change of pH of the solutions. The conclusions reached are very similar to those put forward by Kahler (1948) for reactions within the system $\text{MgO-MgSO}_4\text{-H}_2\text{O}$. The reactions which take place within the systems $\text{MgO-CaCl}_2\text{-H}_2\text{O}$, $\text{CaO-MgCl}_2\text{-H}_2\text{O}$, $\text{Ca(OH)}_2\text{-MgCl}_2\text{-H}_2\text{O}$, $\text{CaO-CaCl}_2\text{-H}_2\text{O}$, and

$Ca(OH)_2$-$CaCl_2$-H_2O, a knowledge of which is important for understanding the mechanism of the new method of removing unsoundness in limes high in magnesium oxide, are briefly studied. Lastly, an account is given of the optical properties of magnesium oxychlorides and of their stabilities when in contact with water, magnesium chloride solutions, and different atmospheres.

II. Experimental Procedures

The compounds formed by reaction between solutions of magnesium or calcium chloride at various concentrations (expressed throughout the paper as weight/volume) and oxides or hydroxides of magnesium and calcium were obtained by allowing 75 ml of solution to act on 1·5 g of solid at various temperatures between 0 and 110 °C while the mixtures were continuously agitated. After a period long enough to establish equilibrium, the mixtures were filtered rapidly and the last traces of solution removed from the precipitate by pressing it between filter papers with a pressure of 24 ton/in^2. It was verified that, by pressing, the precipitates were obtained with a negligible amount of magnesium chloride (less than 0·02 per cent. of $MgCl_2$ was detected in the leachate after washing alternately with anhydrous ethanol and acetone).

All the products were chemically analysed and selected samples were examined by the X-ray powder method and differential thermal analysis to identify the compounds present. Chemical analysis usually showed that the number of water molecules was higher than 8 for the 3- and 5-forms, 4 for the 2-form, and 5 for the 9-form (values established by Walter-Lévy and her co-workers), but since the excess water does not cause any differences in the X-ray patterns of the materials it must be merely adsorbed on the surface of the finely divided particles. Samples of pure phases were examined beneath a petrological microscope to determine their optical properties.

For the system MgO-$MgCl_2$-H_2O the hydrogen ion concentrations of 20 ml of $MgCl_2$ solutions of various concentrations between 10 and 40 per cent. and temperatures between 0 and 77 °C were measured with Universal indicator papers immediately upon the addition of 0·4 g of MgO and during the reaction.

Calorimetric measurements were made by treating 40 g of each of magnesium oxide, calcium oxide, and calcined dolomite with 1 l. of water or salt solutions in a vacuum flask kept in a water-bath at a controlled temperature of 38 °C. Throughout the experiment the contents of the flask were stirred continuously. The rise in temperature of the mixture was recorded automatically by a thermocouple and recording galvanometer. The results were corrected for the heat lost by transfer to the surrounding medium. For certain reactions the experiments were repeated and samples of the products withdrawn from the solution during the reaction and analysed by chemical, X-ray, and D.T.A. methods.

The stabilities of the 3- and 5-forms of magnesium oxychlorides in different atmospheres were studied by recording the changes in weight of samples stored for long periods in air under room conditions, in carbon dioxide-free air at 95 per cent. relative humidity, and in carbon dioxide at 33 and 79 per cent. relative humidity.

III. Chemistry of the Oxychlorides

(*a*) *The System MgO-$MgCl_2$-H_2O*

The results for the system MgO-$MgCl_2$-H_2O are illustrated graphically in Figure 1, where the $Mg(OH)_2$: $MgCl_2$ ratio of the reaction product is plotted for each of the solution concentrations and temperatures studied. They show that a distinction can be made between compounds formed below and above a temperature of 100 °C. On the low temperature side two lines can be drawn representing the minimum concentration of the solution at all temperatures

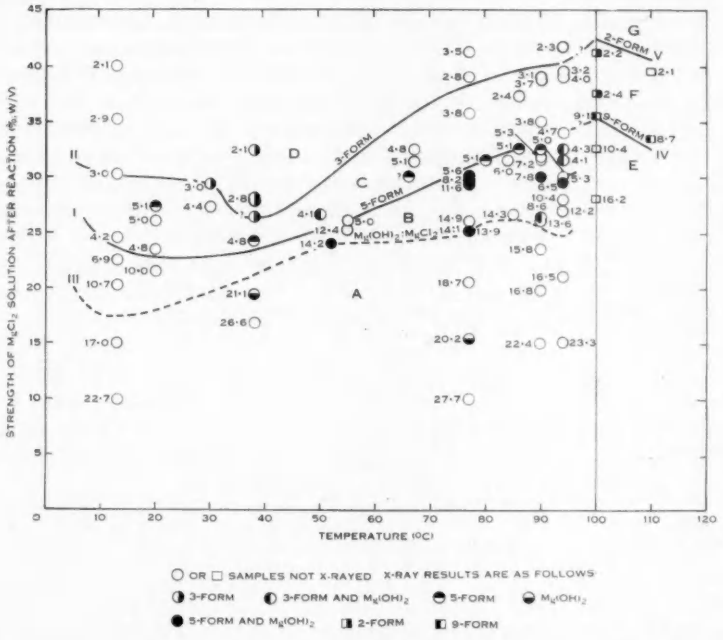

Fig. 1.—Phase equilibria in the system MgO-$MgCl_2$-H_2O. The $Mg(OH)_2$: $MgCl_2$ ratio is given for precipitates found at different conditions of temperature and strength of $MgCl_2$ solution. Curve I, conditions for formation of pure $5Mg(OH)_2.MgCl_2.8H_2O$; II, pure $3Mg(OH)_2.MgCl_2.8H_2O$; IV, pure $9Mg(OH)_2.MgCl_2.5H_2O$; V, pure $2Mg(OH)_2.MgCl_2.4H_2O$. Curve III has been drawn at a $Mg(OH)_2$: $MgCl_2$ ratio of 14 ideally a 50 per cent. mixture of $5Mg(OH)_2.MgCl_2.8H_2O$ and $Mg(OH)_2$. The crystalline products found in the various fields are as follows : *A*, $Mg(OH)_2$; *B*, 5-form and $Mg(OH)_2$; *C*, 5-form or a mixture of 3-form and $Mg(OH)_2$; *D*, 3-form ; *E*, 9-form and $Mg(OH)_2$; *F*, 9- or 2-form ; *G*, 2-form.

at which pure $5Mg(OH)_2.MgCl_2.8H_2O$ (I, Fig. 1) and pure $3Mg(OH)_2.MgCl_2.8H_2O$ (II, Fig. 1) form. On the high temperature side a similar pair of lines has been drawn for pure $9Mg(OH)_2.MgCl_2.5H_2O$ (IV, Fig. 1) and pure $2Mg(OH)_2.MgCl_2.4H_2O$ (V, Fig. 1). Since phase formation must be continuous on either side of 100 °C, curves II and V and I and IV have been joined by dotted lines. The join for the latter departs from the experimental data

presented and indicates the need for more precise work in this region. The four forms of oxychloride are all crystalline and give X-ray powder patterns identical with those published by Walter-Lévy and de Wolff (1949), de Wolff and Walter-Lévy (1949, 1953), and Walter-Lévy and Bianco (1951). In Figure 1 another line has been drawn (curve III) at a $Mg(OH)_2 : MgCl_2$ ratio of 14 representing chemically a mixture of 50 per cent. $5Mg(OH)_2.MgCl_2.8H_2O$ and $Mg(OH)_2$.

Below 100 °C curves I, II, and III divide Figure 1 into four fields *A*, *B*, *C*, and *D* which are progressively crossed with increasing concentration of the magnesium chloride solution. In field *A* the $Mg(OH)_2 : MgCl_2$ ratio of the reaction products varies continuously from infinity for pure $Mg(OH)_2$ to 14 at curve III. X-ray analysis shows that $Mg(OH)_2$ is the only crystalline phase present, although differential thermal analysis, to be discussed later, indicates that an oxychloride has formed with either too fine a particle size or too ill-defined a structure to diffract X-rays. In field *B* the $Mg(OH)_2 : MgCl_2$ ratio varies continuously from 14 to 5 and X-ray analysis shows a mixture of the 5-form and $Mg(OH)_2$ with the content of the latter decreasing to zero at curve I. The reaction products in field *C* have a $Mg(OH)_2 : MgCl_2$ ratio which falls from 5 at curve I to 3 at curve II. In the lower part of field *C* there may be a limited region in which the 5-form is stable, but there are insufficient data to delineate it. Most samples in field *C* are a mixture of $Mg(OH)_2$ and the 3-form. In field *D* the $Mg(OH)_2 : MgCl_2$ ratio of the reaction product varies from 3 to 2 with a tendency for values to be close to whole numbers. However, X-ray analysis has shown that the 3-form is the only crystalline compound formed in the field so that the apparent 2-form would appear to be a solid solution of $MgCl_2$ in $3Mg(OH)_2.MgCl_2.8H_2O$ in a pseudo-stoichiometric amount. At 0 °C $Mg(OH)_2$ forms at all concentrations, although at the very highest (40 per cent.) the product contains a small amount of $MgCl_2$ indicating either the formation of an amorphous oxychloride or the existence of a solid solution of $MgCl_2$ in $Mg(OH)_2$.

At and above 100 °C curves IV and V divide Figure 1 into three fields *E*, *F*, and *G* which are progressively crossed with increasing concentration of the magnesium chloride solution. In field *E* the reaction product should be a mixture of the 9-form and $Mg(OH)_2$ (cf. field *B* which contains a mixture of the 5-form and $Mg(OH)_2$). It is probable that the 2-form occupies the greater part of field *F* and that the 9-form is restricted to a small region adjacent to curve IV. In field *G* at $Mg(OH)_2 : MgCl_2$ ratios less than 2, the 2-form is still the stable phase. However, too little data are available on the high temperature forms to be certain of these interpretations of fields *E*, *F*, and *G*.

(*b*) *The Systems* MgO-$CaCl_2$-H_2O, CaO-$MgCl_2$-H_2O, *and* $Ca(OH)_2$-$MgCl_2$-H_2O

The reactions between magnesium oxide and calcium chloride solutions and calcium oxide, or hydroxide, and magnesium chloride solutions have been studied at temperatures of 38 and 94 °C. As with the system MgO-$MgCl_2$-H_2O the $Mg(OH)_2 : MgCl_2$ ratio of the compounds formed decreases with increasing concentration of $CaCl_2$, or $MgCl_2$, solutions (Tables 1 and 2). In these tables it can be seen that the only oxychloride recognized by X-ray analysis is the 3-form

TABLE 1

REACTION PRODUCTS FORMED IN THE SYSTEM MgO-$CaCl_2$-H_2O AT TEMPERATURES OF 38 AND 94 °C

Temp. (°C)	Final Strength of $CaCl_2$ Solution (% w/v)	Reaction Time (days)	Composition of Solid Phase							
			Molecular Ratio					Components		
			CO_2	CaO	H_2O	MgO	$MgCl_2$	Chemical Analysis	Wt.* (%)	X-Ray Analysis
38	13·12	25	5·2	6·2	42·1	34·2	1·0	$5Mg(OH)_2.MgCl_2.7H_2O$	18	‡
								$Mg(OH)_2$	61	
								$Ca(OH)_2$	3	
								$CaCO_3$†	18	
	16·80	8	2·4	3·6	41·2	29·2	1·0	$5Mg(OH)_2.MgCl_2.10H_2O$	25	No recognizable oxychloride
								$Mg(OH)_2$	60	$Mg(OH)_2$
								$Ca(OH)_2$	6	—
								$CaCO_3$†	9	$CaCO_3$
		12	5·0	8·2	36·6	22·7	1·0	$5Mg(OH)_2.MgCl_2.11H_2O$	25	‡
								$Mg(OH)_2$	45	
								$Ca(OH)_2$	9	
								$CaCO_3$†	21	
	28·50	3	2·8	2·8	24·0	17·9	1·0	$3Mg(OH)_2.MgCl_2.6H_2O$	24	3-form $Mg(OH)_2$
								$Mg(OH)_2$	56	
								$CaCO_3$†	19	$CaCO_3$
94	28·60	8	7·8	18·5	25·6	4·9	1·0	$3Mg(OH)_2.MgCl_2.10H_2O$	21	No recognizable oxychloride
								$Mg(OH)_2$	5	$Mg(OH)_2$
								$Ca(OH)_2$	37	Not recognized
								$CaCO_3$†	37	$CaCO_3$

* From chemical analysis.

† Probably formed by carbonation of $Ca(OH)_2$ from solution during filtration.

‡ Not examined.

TABLE 2

REACTION PRODUCTS FORMED IN THE SYSTEM CaO-$MgCl_2$-H_2O AT TEMPERATURES OF 38 AND 94 °C AND IN THE SYSTEM $Ca(OH)_2$-$MgCl_2$-H_2O AT A TEMPERATURE OF 38 °C

Temp. (°C)	Material Used	Final Strength of $MgCl_2$ Solution (% w/v)	Reaction Time (days)	Composition of Solid Phase							
				Molecular Ratio					Components		
				CO_2	CaO	H_2O	MgO	$MgCl_2$	Chemical Analysis	Wt.* (%)	X-Ray Analysis
38	$Ca(OH)_2$	13·20	3	16·0	16·4	73·9	55·7	1·0	$5Mg(OH)_2.MgCl_2.16H_2O$	13	Ill-defined 3-form ?
									$Mg(OH)_2$	56	$Mg(OH)_2$
									$CaCO_3$†	30	‡
	CaO	26·60	1	0·4	1·2	22·8	13·8	1·0	$3Mg(OH)_2.MgCl_2.8H_2O$	37	3-form
									$Mg(OH)_2$	57	$Mg(OH)_2$
									$Ca(OH)_2$	6	—
	$Ca(OH)_2$	27·80	3	6·2	7·1	31·6	21·8	1·0	$3Mg(OH)_2.MgCl_2.9H_2O$	20	3-form
									$Mg(OH)_2$	50	$Mg(OH)_2$
									$Ca(OH)_2$	3	—
									$CaCO_3$†	27	$CaCO_3$
94	CaO	22·10	1	17·1	18·6	22·6	7·5	1·0	$3Mg(OH)_2.MgCl_2.13H_2O$	19	||
									$Mg(OH)_2$	11	
									$Ca(OH)_2$	6	
									$CaCO_3$†	64	
		26·60	2	1·7	1·7	22·9	12·0	1·0	$3Mg(OH)_2.MgCl_2.11H_2O$	39	3-form
									$Mg(OH)_2$	44	$Mg(OH)_2$
									$CaCO_3$†	17	$CaCO_3$

* From chemical analysis.

† Probably formed by carbonation of $Ca(OH)_2$ from solution during filtration.

‡ Not present in sample X-rayed.

|| Not examined.

but it is to be expected that there would be conditions in the system MgO-$CaCl_2$-H_2O under which the 5-form may exist. In the two systems there is an initial reaction between the salt and the solid to give, in the case of the system MgO-$CaCl_2$-H_2O, $MgCl_2$ and, in the case of the system CaO-$MgCl_2$-H_2O, $Mg(OH)_2$, and these react with excess oxide and chloride respectively, to give an oxychloride.

(c) *The Systems CaO-$CaCl_2$-H_2O and $Ca(OH)_2$-$CaCl_2$-H_2O*

Reactions in the systems CaO-$CaCl_2$-H_2O at temperatures of 38 and 94 °C and $Ca(OH)_2$-$CaCl_2$-H_2O at a temperature of 38 °C have been studied at different concentrations of the calcium chloride solutions. The results (Table 3) show that the reaction products for both systems are a mixture of a calcium oxychloride, $3Ca(OH)_2.CaCl_2.xH_2O$ (x varying from 8 to 13 but not affecting the structure) and $Ca(OH)_2$, and that they form faster when CaO is the solid phase. For the system CaO-$CaCl_2$-H_2O the amount of the oxychloride increases with the concentration of the chloride solution.

IV. Reaction Processes

At an early stage in the investigation measurements were made of the heat generated when magnesium oxide, calcium oxide, and calcined dolomite were added to water or salt solutions. The experiments were discontinued when the results obtained had indicated that oxychlorides were being formed under certain conditions. Subsequently it was realized that the experiments once interpreted would yield valuable information on the mechanism of oxychloride formation, so the early work was repeated and the reaction products subjected to chemical, X-ray, and differential thermal analyses to establish the composition of the solid phase at various stages throughout the reaction. In other experiments the change of hydrogen ion concentrations was measured during reactions between MgO and $MgCl_2$ solutions of different concentrations, and the amounts of dissolved MgO in solution determined immediately upon adding the solid to the liquid. The additional data have allowed some interesting ideas to be formulated on the reaction processes within the MgO-$MgCl_2$-H_2O system.

(a) *Oxides with Water*

The increases in temperature with time for reactions between magnesium oxide and calcium oxide and water are illustrated in Figure 2. The reaction between calcium oxide and water produces a greater temperature rise and is much more rapid than that between magnesium oxide and water. The shape of the curve for the two oxides (and for other systems to be discussed later) depends on the activation energy, the heat capacity of the system, the concentration of the reactant and the commencing temperature of the reaction (Bredig and Epstein 1904) and so need not be significant but that for magnesium oxide and water is very similar to one published by Kahler (1948). However, Kahler (1948) was able to observe a small but rapid initial rise in temperature, an accompanying high conductivity, and an increased solubility of MgO in water

TABLE 3

REACTION PRODUCTS FORMED IN THE SYSTEM CaO-$CaCl_2$-H_2O AT TEMPERATURES OF 38 AND 94 °C AND IN THE SYSTEM $Ca(OH)_2$-$CaCl_2$-H_2O AT A TEMPERATURE OF 38 °C

Temp. (°C)	Material Used	Final Strength of $CaCl_2$ Solution (% w/v)	Reaction Time (days)	Composition of Solid Phase						
				Molecular Ratio				Components		
				H_2O	CO_2	CaO	$CaCl_2$	Chemical Analysis	Wt.* (%)	X-Ray Analysis
38	$Ca(OH)_2$	17·00	3	49·4	9·0	45·4	1·0	$3Ca(OH)_2.CaCl_2.13H_2O$ $Ca(OH)_2$ $CaCO_3$†	15 62 23	‡
	$Ca(OH)_2$	27·80	3	22·1	2·3	13·7	1·0	$3Ca(OH)_2.CaCl_2.10H_2O$ $Ca(OH)_2$ $CaCO_3$†	37 48 15	‡
	CaO	27·80	1	17·8	0·7	9·3	1·0	$3Ca(OH)_2.CaCl_2.10H_2O$ $Ca(OH)_2$ $CaCO_3$†	52 38 10	3-form $Ca(OH)_2$
	CaO	27·80	5	15·1	Traces	4·3	1·0	$3Ca(OH)_2.CaCl_2.11H_2O$ $Ca(OH)_2$	88 12	‡
94	CaO	29·14	1	15·2	Traces	4·2	1·0	$3Ca(OH)_2.CaCl_2.11H_2O$ $Ca(OH)_2$	88 12	3-form $Ca(OH)_2$

* From chemical analysis.

† Probably formed by carbonation of $Ca(OH)_2$ from solution during filtration.

‡ Not examined.

(35 mg/l). As the hydration of the oxide proceeded the conductivity fell and the solubility of the MgO assumed its normal value (8·6 mg/l). These phenomena may be important in processes to be discussed in the next section.

(*b*) *Oxides with Salt Solutions*

In discussing reactions between pure oxides and salt solutions it is convenient to consider firstly, the processes that take place immediately the oxide is added to the solution and secondly, subsequent processes.

(i) *Processes Immediate upon adding MgO to $MgCl_2$ Solutions.*—Measurements of the pH of solutions of $MgCl_2$ of different concentrations at temperatures of 0, 20, 38, and 77 °C immediate upon the addition of MgO to the solution are set out in Table 4. The results show that at all temperatures there is a change,

TABLE 4

HYDROGEN ION CONCENTRATIONS OF $MgCl_2$ SOLUTIONS OF VARIOUS CONCENTRATIONS (ORIGINAL pH 5·5) AND TEMPERATURES IMMEDIATELY AFTER THE ADDITION OF 20 G/L OF MgO (INITIAL) AND AFTER THE COMPLETION OF REACTION (FINAL)

Nominal Concn. of $MgCl_2$ (% w/v)	0 °C	20 °C		38 °C		77 °C	
		Initial	Final	Initial	Final	Initial	Final
10	10·5	10·0	7·8	10·0	8·5	10·0	9·1
15	9·8	10·0	7·6	N.D.	8·0	N.D.	N.D.
20	9·1	9·5	7·3	9·6	7·6	9·7	8·8
25	8·8	N.D.*	7·0	N.D.	7·3	N.D.	N.D.
30	8·2	8·5	6·7	8·5	7·0	8·5	6·4
35	7·6	N.D.	6·1	N.D.	5·8	N.D.	N.D.
40	5·8	8·3	5·5	8·2	5·5	8·2	5·5

* N.D., not determined.

once MgO is added, from pH 5·5, the pH of magnesium chloride solution itself, to higher values depending upon the concentration of the solution. At a temperature of 0 °C and high concentrations of $MgCl_2$ solutions the change is slight and difficult to explain, but between solutions of concentration of 10 and 40 per cent. $MgCl_2$ there is a difference of pH of approximately 5, representing a difference in concentration of Mg ions in solution of the order of 10^{10}. Further, the liquids from two solutions of 10 and 40 per cent. $MgCl_2$ at room temperature were separated from their solids in a supercentrifuge, within a few minutes of mixing, and analysed for free MgO. There was not a sufficient increase in the solubility of $Mg(OH)_2$ in $MgCl_2$ to explain the high pH values. However, the content of MgO in solution is much higher than expected (in water the solubility of MgO is 8·6 mg/l (see Kahler 1948) 3·2 g/l for a 10 per cent. $MgCl_2$ solution, and 9·0 g/l for a 40 per cent. solution. It is to be noted that Kahler has also observed an increase in the solubility of MgO in $MgSO_4$ solution of the order of 0·4 g/l under somewhat similar conditions. The analytical values for magnesium oxide

and chloride were obtained gravimetrically in the present work as follows: total MgO was found by evaporating the solution in the presence of Hg_2O and igniting, and chlorine by precipitating as AgCl; MgO in solution is that remaining after allowance is made for $MgCl_2$. When the results were checked volumetrically by direct titration of the undiluted solution with acid as suggested by Chassevent (1934) much lower figures were obtained (1·4 g/l for a 10 per cent. solution). However, if a measured surplus of 0·1N HCl is added and the solution back titrated with 0·1N NaOH using methyl orange as an indicator, figures are obtained which agree with the gravimetric results, indicating that there is in solution, besides free MgO, an additional source of MgO, such as a complex ion, which is decomposed by excess acid. It is thus concluded that when MgO is added to $MgCl_2$ solutions a complex ion is formed which effectively removes Mg ions from solution and produces changes in pH which cannot be explained by accepted physical chemical laws. It is not clear whether the complex ion forms first or is preceded by the formation of $Mg(OH)_2$ which, as Kahler (1948) has shown for reactions with water, takes place rapidly and possesses an enhanced solubility. In the latter case the complex ion would form in a saturated solution of $Mg(OH)_2$. The conclusions derived here for the system $MgO\text{-}MgCl_2\text{-}H_2O$, from observations of change of pH and solubility of MgO in $MgCl_2$, are paralleled by those drawn by Kahler (1948) for the system $MgO\text{-}MgSO_4\text{-}H_2O$ from observations of conductivity and solubility of MgO in $MgSO_4$. Kahler was forced to postulate an occurrence in solution of a complex salt of the type $[Mg\{Mg(OH)_2\}_n]SO_4$.

(ii) *Subsequent Processes.*—Adiabatic calorimetric studies have been carried out for reactions between magnesium oxide and magnesium chloride and calcium chloride solutions at a temperature of 38 °C, and the curve of the temperature rise has been correlated with compound formation, by examining the reaction product at intervals by chemical, X-ray, and D.T.A. methods. The rises in temperature for reactions between MgO and 5 per cent. $MgCl_2$ and $CaCl_2$ solutions are shown in Figure 2 by curves *C* and *F*, respectively. The shape of the curves is very similar to that produced by reaction between MgO and water and since no oxychloride was found at such low concentration of solutions within the system $MgO\text{-}MgCl_2\text{-}H_2O$, it is concluded that the temperature rise in the present experiments is solely due to the hydration of MgO to $Mg(OH)_2$. On the other hand for reactions between MgO and $MgCl_2$ and $CaCl_2$ solutions of 19 per cent. concentration, the shape of the curves, Figure 2, *D* and *F* respectively, strongly suggest that oxychlorides have formed in addition. X-ray examination of the product obtained after 2 hr and 24 hr under conditions similar to *D*, Figure 2 (19·4 per cent. $MgCl_2$ solution) showed the presence of only $Mg(OH)_2$ but chemical analysis indicates a $Mg(OH)_2 : MgCl_2$ ratio of 19 and D.T.A. of the product yields a curve (*F*, Fig. 3) which is interpreted as representing a mixture of $Mg(OH)_2$ and an ill-formed oxychloride. If the curve of $Mg(OH)_2$ (*D*, Fig. 3) is subtracted from that of *F* (Fig. 3) on the basis of the latter containing 60 per cent. $Mg(OH)_2$ by weight, a curve *G* (Fig. 3) is obtained, which is more like that of pure $5Mg(OH)_2.MgCl_2.8H_2O$ (*E*, Fig. 3) than pure $3Mg(OH)_2.MgCl_2.8H_2O$

(*A*, Fig. 3). It is to be noted that the single endothermic peak between 100 and 200 °C for *F* (Fig. 3) represents, by contrast with well-crystallized oxychlorides *A* and *E* (Fig. 3), loosely bound and poorly organized water layers, thus confirming the non-crystallinity deduced from X-ray examination. It will be seen from the equilibria fields of Figure 1 that at a temperature of 38 °C, the reaction product at a concentration of 19 per cent. $MgCl_2$ correctly falls into field *A*. For reactions between MgO and a $MgCl_2$ solution of 25 per cent. concentration the curve of temperature rise (*E*, Fig. 2) might be interpreted at first glance as

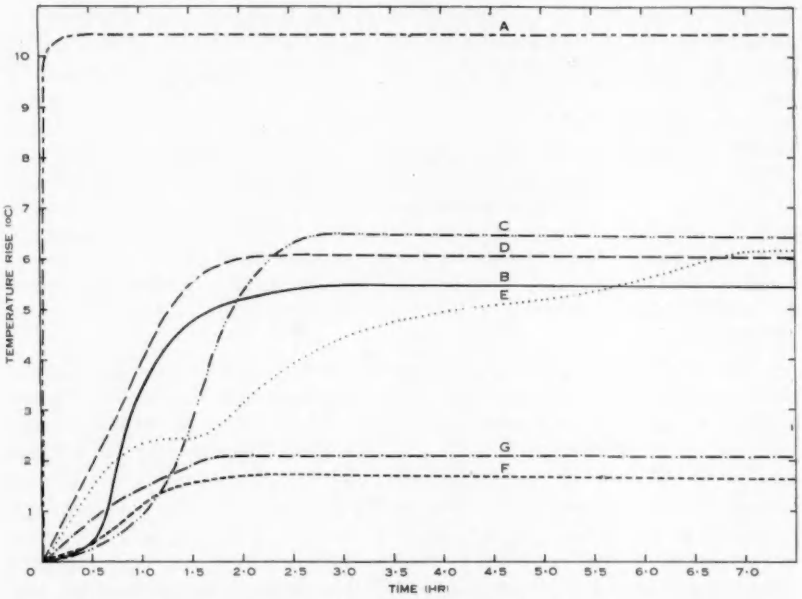

Fig. 2.—Temperature rise during reaction of magnesium and calcium oxides with water and salt solutions.

A, CaO with water ; *B*, MgO with water ; *C*, MgO with 5 per cent. $MgCl_2$ solution ; *D*, MgO with 19 per cent. $MgCl_2$ solution ; *E*, MgO with 25 per cent. $MgCl_2$ solution ; *F*, MgO with 5 per cent. $CaCl_2$ solution ; *G*, MgO with 19 per cent. $CaCl_2$ solution.

representing the occurrence of consecutive reactions but this is not confirmed by other data. X-ray examination of the product obtained after $1\frac{3}{4}$, $4\frac{1}{4}$, and $7\frac{1}{2}$ hr under similar conditions (24 per cent. $MgCl_2$ solution) showed only $Mg(OH)_2$, whereas that taken after 24 hr was a mixture of $Mg(OH)_2$ and the 3-form. Once again, from D.T.A., the composition of the reaction products obtained after the shorter intervals could be interpreted as a mixture of $Mg(OH)_2$ and an ill-formed oxychloride (*B*, Fig. 3) which was, this time, more like the 3-form (*A*, Fig. 3) than the 5-form (*E*, Fig. 3). Chemical analysis indicates a $Mg(OH)_2 : MgCl_2$

ratio of 12 for all samples up to a reaction time of 24 hr, but since a ratio of between 3 and 5 is expected under the experimental conditions (Fig. 1), equilibrium would not appear to have been established.

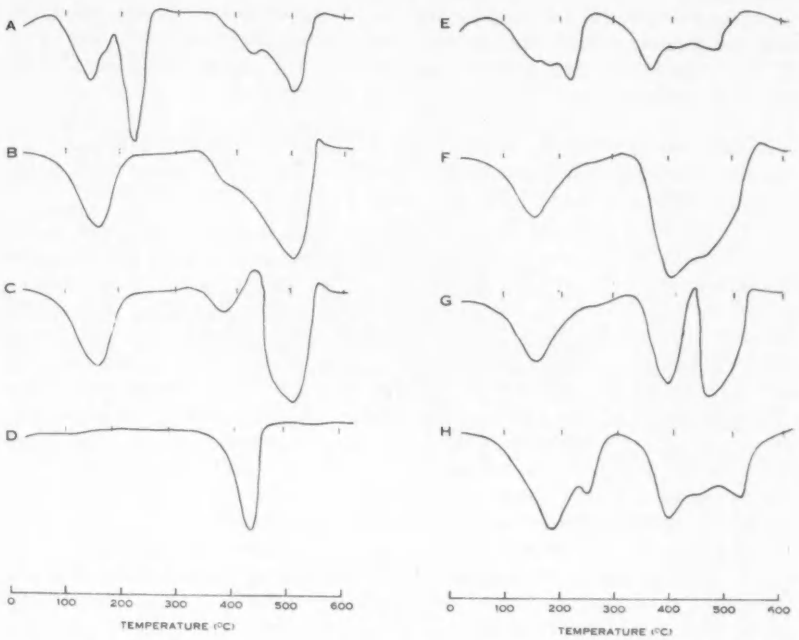

Fig. 3.—Differential thermal analysis curves of magnesium oxychlorides and magnesium hydroxide.

A, pure 3-form, $3Mg(OH)_2.MgCl_2.7{\cdot}7H_2O$. Weight of sample 0·15 g, sensitivity 100 μV full-scale deflection.

B, product formed in calorimeter at 38 °C after 4½ hr from reaction between 40 g of MgO and 1 l. of $MgCl_2$ solution of 24 per cent. concentration. Weight of sample 0·4 g, sensitivity 200 μV full-scale deflection.

C, curve *B* from which curve *D*, that of pure $Mg(OH)_2$ has been subtracted on the basis that the latter forms 56 per cent. by weight of the former.

D, pure $Mg(OH)_2$. Weight of sample 0·28 g, sensitivity 200 μV full-scale deflection.

E, pure 5-form, $5Mg(OH)_2.MgCl_2.7{\cdot}9H_2O$. Weight of sample 0·15 g, sensitivity 100 μV full-scale deflection.

F, product formed in calorimeter at 38 °C, after 2 hr from reaction between 40 g of MgO and 1 l. of $MgCl_2$ solution of 19 per cent. concentration. Weight of sample 0·54 g, sensitivity 200 μV full-scale deflection.

G, curve *F* from which curve *D*, that of pure $Mg(OH)_2$, has been subtracted on the basis that the latter forms 60 per cent. by weight of the former.

H, product formed in calorimeter at 38 °C, after 1 hr from reaction between 40 g of calcined dolomite and 1 l. of $MgCl_2$ solution of 23 per cent. concentration. Weight of sample 0·54 g, sensitivity 200 μV full-scale deflection.

Although calorimetric measurements were not made for reactions between MgO and $MgCl_2$ solutions of concentration greater than 25 per cent. the reaction products were examined in detail at intervals from solutions of 30 per cent. $MgCl_2$ and conditions otherwise similar to those used in those experiments. X-ray examination of the product after $1\frac{1}{2}$ hr showed the presence of $Mg(OH)_2$ and the 5-form. After 5 hr the $Mg(OH)_2$ had largely disappeared and after $3\frac{1}{2}$ days the 3-form had replaced the 5-form. The results are confirmed by chemical analyses which show a $Mg(OH)_2 : MgCl_2$ ratio of 15·5 after $1\frac{1}{2}$ hr, 5·3 after 5 hr, and 3·0 after $3\frac{1}{2}$ days. The early formation of the 5-form at concentrations at which the 3-form is stable (the 3-form is stable at a concentration of 30 per cent. $MgCl_2$ used in the experiment Fig. 1) has already been noted by Feitknecht and Held (1944) and other workers.

The reaction processes at 38 °C between MgO and $MgCl_2$ solutions of 19, 24, and 30 per cent. concentrations, just discussed, cover the formation of the reaction product for all fields of Figure 1, with the exception of *B*, where a crystalline oxychloride of the 5-form crystallizes with $Mg(OH)_2$. The results indicate that in the formation of magnesium oxychlorides in the system $MgO\text{-}MgCl_2\text{-}H_2O$ a reaction probably takes place between early formed $Mg(OH)_2$ and a complex ion yielding an amorphous oxychloride, which may show similarities to either the 5-form or the 3-form. Above a certain concentration, depending on the temperature, the amorphous oxychloride slowly crystallizes either to the 5-form or the 3-form. In the latter at high concentrations it is always preceded by the former. In general, the content of $Mg(OH)_2$ is reduced as the oxychlorides crystallize suggesting that they form from it by reactions in the solid state. It is to be noted that in the course of the reactions the pH drops as indicated in Table 4. The lower pH measurements observed with increasing concentration of $MgCl_2$ solution, also illustrated in Table 4, show that at any temperature the 5-form is stable in a more basic medium than the 3-form.

(*c*) *Calcined Dolomite with Water and Salt Solutions*

Adiabatic calorimetric studies have also been made of the reactions which take place between calcined dolomitic lime and water and salt solutions. The rise in temperature for water, 10 and 23 per cent. $MgCl_2$ solutions, and 10 and 21 per cent. $CaCl_2$ solutions lies between 6 and 7 °C and is always rapid (it is more rapid for $CaCl_2$ than for $MgCl_2$ solutions), equilibrium being established in less than an hour. Since all the curves are similar and the significance of minor details uncertain, they are not reproduced here. In the case of the reaction of dolomite with water a rapid temperature rise of 6 °C indicates that the CaO, which amounts to 53·3 per cent. by weight, hydrates completely but the MgO only partly. This is explained by the magnesium oxide having been rendered partly inert by the high temperature (1100 °C) at which the dolomite was calcined. The product formed, after 1 and 24 hr for a solution of 23 per cent. $MgCl_2$ and after $\frac{1}{2}$ and 24 hr for a solution of 21 per cent. $CaCl_2$, was examined by the X-ray method. With the $MgCl_2$ solution it was a mixture of the 5-form, MgO, and $Mg(OH)_2$ and with the $CaCl_2$ solution a mixture of the 3-form, MgO, and $Ca(OH)_2$ and the compositions were the same after 24 hr as after the shorter

intervals. Since $Ca(OH)_2$ does not appear in the solid phase in reaction between the dolomite and the $MgCl_2$ solution it must be assumed that it reacts with $MgCl_2$ to form $CaCl_2$ and $Mg(OH)_2$ as discussed in an earlier section. In reactions between the dolomite and the $CaCl_2$ solution, $Ca(OH)_2$ appears in the solid phase because of the high concentration of Ca ions in solution. The occurrence of the two forms of oxychlorides is to be expected from the results for the systems MgO-$CaCl_2$-H_2O and CaO-$MgCl_2$-H_2O.

V. Optical Properties

The optical properties have been examined for all pure oxychloride forms discussed in the present paper. The magnesium oxychlorides are very poorly crystalline and the calcium oxychloride very unstable; hence, only a limited number of data can be obtained. The 3-form occurs as a gel-like aggregate (Plate 1, Fig. 1) of minute crystals which are irregular in shape and of very low birefringence. The mean refractive index lies between 1·505 and 1·510. The 5-form (Plate 1, Fig. 2) tends to be more crystalline, forming well-shaped, weakly birefringent needles approximately 0·01 mm long. Their extinction is parallel and optical elongation negative; the mean refractive index is 1·525. Both the 2- and the 9-forms occur as well-shaped crystals similar to those of the 5-form. The 3-form of calcium oxychloride forms long, highly birefringent crystals with a good cleavage perpendicular to their length. Refractive indices were not measured because the crystals were unstable when in contact with the immersion liquids available.

VI. Stability of Magnesium Oxychlorides

(*a*) *Stability in Contact with Water and Magnesium Chloride Solutions*

The stabilities of pure preparations of the 3- and 5-forms in contact with water and magnesium chloride solutions were studied at room temperature (approx. 13 °C) and at 77 °C. The results have been plotted in Figure 4 on the equilibria diagram of Figure 1. It is clear that the two sets of results do not agree. It is to be expected that both forms will hydrolyse when immersed in water, or dilute magnesium chloride solutions, but the concentrations at which phases transform from one to the other are very much lower than for the phase equilibria established in Figure 1. The explanation for this is not clear. Although the 3-form hydrolyses in water like the 5-form it is stable over a wider range of concentrations. This greater stability is borne out also by data presented below on their relative behaviour in different atmospheres, and in data on the decomposition in air of high temperature phases of each form (Cole and Demediuk 1955).

The behaviour of the 9-form when kept in contact with salt solutions is also unusual. At room temperature, in 20 and 30 per cent. $MgCl_2$ solutions the ratio of $Mg(OH)_2$: $MgCl_2$ changed from 9 to 6 and 4 respectively, without any change in X-ray patterns. It seems that the structure of the 9-form is sufficiently defective to hold large quantities of non-structural magnesium chloride within the crystal lattice. There is evidence, from the existence of a $Mg(OH)_2$: $MgCl_2$ ratio of 2 in the phase equilibria of the system MgO-$MgCl_2$-H_2O at temperatures below 100 °C, that the 3-form has a defective structure also.

(b) Stability of Magnesium Oxychlorides in Different Atmospheres

The stabilities of pure preparations of the 3- and the 5-forms were studied also in different atmospheres by recording the changes in weight over a period of 100 days. Both materials suffer little decomposition in air at 13 °C and 65 per cent. relative humidity (curves I and II, Fig. 5), although the 5-form has increased its weight by 9·5 per cent. after 60 days. However, other data (Cole and Demediuk 1955) show that both forms change after a long period to basic magnesium chlorocarbonate ($Mg(OH)_2.2MgCO_3.MgCl_2.6H_2O$). The 3-form also is relatively stable in a CO_2 atmosphere at 33 per cent. relative humidity (curve

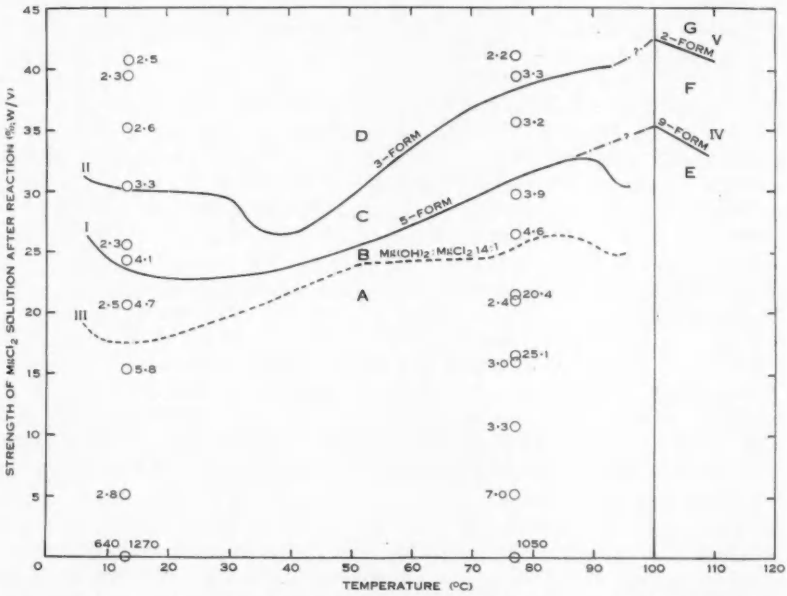

Fig. 4.—Stabilities of samples of pure $3Mg(OH)_2.MgCl_2.8H_2O$ and pure $5Mg(OH)_2.MgCl_2.8H_2O$ when in contact with magnesium chloride solutions of various concentrations at temperatures of 13 and 77 °C. The $Mg(OH)_2 : MgCl_2$ ratios of the products after a reaction time of 3 days have been plotted on the equilibria diagram of Figure 1. ○ The ratios to the left refer to the 3-form and those to the right to the 5-form.

III, Fig. 5), whereas the 5-form increased its weight by 14 per cent. in 5 days and reached a maximum of 19 per cent. after 45 days (curve IV, Fig. 5). However, in a CO_2-atmosphere at 79 per cent. relative humidity both forms change (curves V and VI, Fig. 5) within a week to basic magnesium chlorocarbonate, as identified by X-ray and chemical analysis. The materials are unstable also when exposed to a CO_2-free atmosphere of 95 per cent. relative humidity (curves VII and VIII, Fig. 5) the decomposition products being $Mg(OH)_2$ and $MgCl_2$. Further data on the behaviour of the oxychlorides in air and after dehydration by heat are to be published separately (Cole and Demediuk 1955).

VII. Conclusions

(1) A detailed examination by chemical and X-ray methods of the compounds formed in the system MgO-$MgCl_2$-H_2O has confirmed the existence of the four magnesium oxychlorides, $9Mg(OH)_2.MgCl_2.5H_2O$, $5Mg(OH)_2.MgCl_2.8H_2O$, $3Mg(OH)_2.MgCl_2.8H_2O$, and $2Mg(OH)_2.MgCl_2.4H_2O$ reported by earlier workers, and has supplied new information on the conditions under which each oxy-

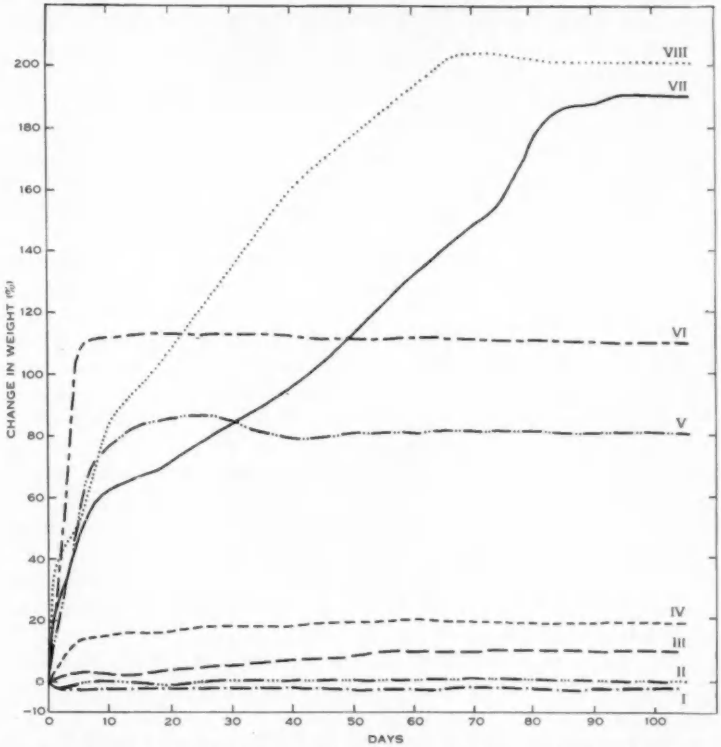

Fig. 5.—Percentage increase in weight with time of exposure of magnesium oxychlorides of the 5- and 3-forms exposed to CO_2 and moisture.
I, 3-form in air; II, 5-form in air; III, 3-form in a CO_2-atmosphere at 33 per cent. relative humidity; IV, 5-form in a CO_2-atmosphere at 33 per cent. relative humidity; V, 3-form in a CO_2-atmosphere at 79 per cent. relative humidity; VI, 5-form in a CO_2-atmosphere at 79 per cent. relative humidity; VII, 3-form in a CO_2-free atmosphere at 95 per cent. relative humidity; VIII, 5-form in a CO_2-free atmosphere at 95 per cent. relative humidity.

chloride forms and is stable. An equilibria diagram has been prepared showing the phases formed in $MgCl_2$ solutions up to concentrations of 45 per cent. and temperatures from 0 to 110 °C. The 5- and 3-forms are precipitated below 100 °C and the 9- and 2-forms at and above 100 °C, the form with the highest $Mg(OH)_2 : MgCl_2$ ratio being in each case stable at lower concentrations.

(2) An examination of the reaction processes involved in the formation of magnesium oxychlorides at temperatures below 100 °C shows complex phenomena. When MgO is first added to a $MgCl_2$ solution there is a marked change in pH, from acid to basic. The solubility also of MgO in the $MgCl_2$ solution is greatly increased. These effects are, it is considered, due to the formation of a complex ion which subsequently reacts with $Mg(OH)_2$, formed by rapid hydration of MgO, to produce amorphous oxychlorides which may show similarities to either the 3- or the 5-form. Above a certain concentration, which is temperature dependent, they slowly crystallize to yield reaction products whose compositions conform to the equilibria diagram.

(3) A preliminary examination of the systems $MgO\text{-}CaCl_2\text{-}H_2O$ and $CaO\text{-}MgCl_2\text{-}H_2O$ at temperatures of 38 and 94 °C, and of the system $Ca(OH)_2\text{-}MgCl_2\text{-}H_2O$ at a temperature of 38 °C, shows that a magnesium oxychloride of the 3-form is produced and of the 5-form is to be expected. It is probable that each system has an equilibrium diagram and a mechanism of oxychloride formation similar to the system $MgO\text{-}MgCl_2\text{-}H_2O$.

(4) In the systems $CaO\text{-}CaCl_2\text{-}H_2O$ and $Ca(OH)_2\text{-}CaCl_2\text{-}H_2O$ at temperatures of 38, 94, and 38 °C respectively, there is only one oxychloride of composition $3Ca(OH)_2.CaCl_2.xH_2O$.

(5) When calcined dolomite reacts with $MgCl_2$ or $CaCl_2$ solutions magnesium oxychlorides of the composition of either the 5- or the 3-form may be produced and it is suggested that this is the explanation for the success of the new method proposed by Demediuk (1952) for the removal of unsoundness in limes high in magnesium oxide.

(6) Observations on the stabilities of magnesium oxychlorides of the 5- and the 3-forms, in contact with water and magnesium chloride solutions and in different atmospheres, show as is to be expected from their conditions of formation, that the 3-form is more stable than the 5-form. In air they both react with CO_2 to form the stable magnesium chlorocarbonate $Mg(OH)_2.2MgCO_3.MgCl_2.6H_2O$. The calcium oxychloride $3Ca(OH)_2.CaCl_2.xH_2O$ is very unstable when removed from solution.

(7) The magnesium oxychlorides all form poorly crystalline needles with low birefringence and mean refractive index between 1·505 and 1·525. Calcium oxychloride by contrast forms large well-crystallized needles.

(8) Of the magnesium oxychlorides both the 9- and the 3-forms can retain appreciable amounts of $MgCl_2$ without modification of structure.

VIII. Acknowledgments

The authors wish to thank their colleagues in this Division, Mr. R. D. Hill for helpful discussion on matters of physical chemistry, Miss A. Feldman for much of the analytical work, and Mr. A. R. Carthew for carrying out the differential thermal analyses and supercentrifuge separations.

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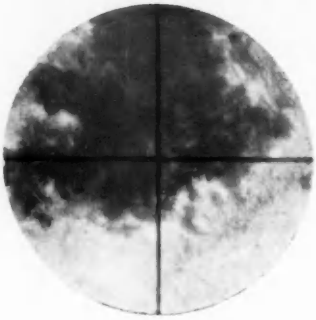
MAGNESIUM AND CALCIUM OXYCHLORIDES



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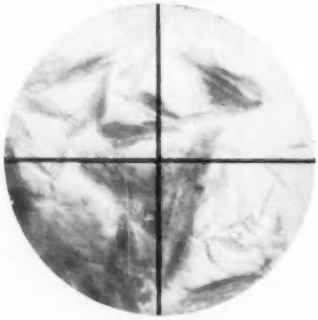

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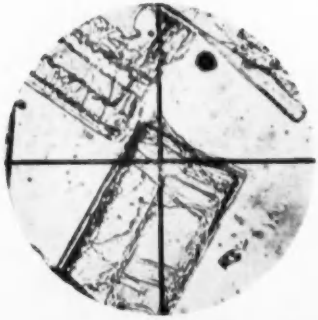

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EXPLANATION OF PLATE 1

Fig. 1.—$3Mg(OH)_2.MgCl_2.8H_2O$ ×400. Formed by reaction between MgO and 28 per cent. $MgCl_2$ solution at 38 °C.

Fig. 2.—$5Mg(OH)_2.MgCl_2.10H_2O$. ×400. Formed by reaction between MgO and 24 per cent. $MgCl_2$ solution at 38 °C.

Fig. 3.—$3Ca(OH)_2.CaCl_2.8H_2O$. ×100. Formed from a hot filtered solution of $Ca(OH)_2$ in 40 per cent. $CaCl_2$ solution.

X-RAY, THERMAL, AND DEHYDRATION STUDIES ON MAGNESIUM OXYCHLORIDES

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Summary

X-ray, differential thermal analysis, and dehydration methods have been used to study the magnesium oxychlorides $3Mg(OH)_2.MgCl_2.8H_2O$ and $5Mg(OH)_2.MgCl_2.8H_2O$ formed at temperatures below 100 °C, and $2Mg(OH)_2 . MgCl_2 . 5H_2O$ and $9Mg(OH)_2.MgCl_2.6H_2O$ formed at temperatures at and above 100 °C. Lower hydrates of the 3-form exist with 5 and 4 molecules of water, results which differ from those of Feitknecht and Held (1944), Feitknecht (1953), and Wehner (1953). It is not clear from the new results whether the lower hydrates for the 5-form have 5 and 3 or 4 and 3 molecules of water, but the latter seems the more likely ; the results of Feitknecht and Held suggested the former. For the 2- and 9-forms a lower hydrate with 2 molecules of water exists. In addition all forms have an anhydrous phase with the crystal structure of $Mg(OH)_2$. The stability of all phases under natural atmospheric conditions is discussed.

I. Introduction

In an investigation of the correction of unsoundness in dolomitic limes through the formation of magnesium oxychlorides by treatment with magnesium chloride solutions (Demediuk, Cole, and Hueber 1955), X-ray, and differential thermal analyses (D.T.A.) were used in characterizing and identifying the compounds formed. The differential thermal curves were most complex and attempts to interpret them have led to a study of the structural changes that occur when oxychlorides are heated and of the stability of all phases under normal conditions of temperature and pressure.

Magnesium oxychlorides are formed by reaction between magnesium oxide and solutions of magnesium chloride. With a solution temperature below 100 °C the compound formed is either $3Mg(OH)_2.MgCl_2.8H_2O$ (3-form) or $5Mg(OH)_2.MgCl_2.8H_2O$ (5-form), at and above 100 °C it is either $2Mg(OH)_2.MgCl_2.4H_2O$ (2-form) or $9Mg(OH)_2.MgCl_2.5H_2O$ (9-form). The terms "low temperature forms" and "high temperature forms" are used in the present paper to designate compounds formed below, and at, or above 100 °C, respectively. Other factors that determine whether the compound is low or high in $Mg(OH)_2$ are discussed by Demediuk, Cole and Hueber (1955).

Dehydration data for the 3-form have been published by Feitknecht and Held (1944), Feitknecht (1953), and Wehner (1953). Although Feitknecht and Held and Wehner agree in their findings the more recent work by de Wolff referred to by Feitknecht (1953) differs in the compositions ascribed to the lower

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hydrates. The present results agree closely with those published by Wehner but differ from his and those of Feitknecht in the number of water molecules assigned to one of the phases. It is considered that the materials used by Wehner had partly decomposed to magnesium chlorocarbonate before he examined them. The X-ray powder patterns of the 3-forms used in this study agree with those published by de Wolff and Walter-Lévy (1953) so that it is not clear why the present results differ from those given by Feitknecht (1953). For the 5-form the results recorded here can be interpreted to confirm the earlier findings of Feitknecht and Held (1944), but the number of water molecules found for the lower hydrates of several samples formed under different conditions has not been integral and so can be interpreted differently ; this form could therefore be studied in more detail. Complete dehydration data for the 2- and 9-forms are published here for the first time, although it is to be noted that Bianco (1951) observed a lower hydrate of the 2-form with 2 molecules of water and published a powder pattern for it, which differs from the one found here for a compound of the same composition.

Because magnesium oxychloride cements are an important building material their stability upon exposure to the atmosphere is of interest. Walter-Lévy and de Wolff (1949) showed that both the 3- and the 5-forms are unstable and alter on standing into magnesium chlorocarbonate which then becomes the stable compound of " Sorel " cement. The physical properties of this compound have recently been discussed by Walter-Lévy, de Wolff, and Soleilhavoup (1953). Walter-Lévy and Bianco (1951) also show that the 2-form is unstable and quickly transforms into the 3-form which then undergoes carbonation ; the 9-form is stable. The stabilities of all forms have been reexamined and the investigation extended to include a study of the behaviour in air of all high temperature phases produced by the dehydration of each form.

Finally, the differential thermal curve of each oxychloride is compared with plots of the differential of the weight-loss curve and interpreted in terms of the high temperature phases shown to exist from dehydration data.

II. Experimental Methods

The various oxychlorides of the 2-, 3-, 5-, and 9-forms, subjected to thermal and dehydration studies in the present investigation, were prepared by methods described by Demediuk, Cole, and Hueber (1955). These original materials represent the phases of each form with the highest number of water molecules. The compositions of those considered in detail are set out in Table 1. In the chemical analyses of the materials the amount of magnesium was measured gravimetrically, the chloride volumetrically, and the water by loss on ignition. However, the number of water molecules quoted in Table 1 has been derived on the assumption that each form has an anhydrous phase ; this procedure has given more consistent results than the use of the analytical figures, since the water content of magnesium oxychlorides is likely to vary with atmospheric conditions and exposure (Demediuk, Cole, and Hueber 1955).

The purity of the original preparations was checked by X-ray powder photographs taken in cameras designed to record high spacings. X-ray analysis

was used also to check the existence of phases formed by heating the samples in dehydration experiments, during D.T.A., and in studying the crystalline changes undergone by magnesium oxychlorides and their high temperature phases upon exposure to air over a prolonged period. Samples were taken for X-ray examination during the running of both automatic D.T.A. and thermobalance experiments and the results checked against the X-ray patterns of small samples that had been heated for long periods (so as to be under equilibrium conditions) in an oven at intervals of approximately 10 °C, from 50 to 250 °C. The latter procedure was found to give the best data for the characteristic X-ray patterns of the high temperature phases. Samples taken from the D.T.A. and thermobalance equipment during running were usually a mixture of phases which could always readily be correlated with the static experiments.

Dehydration data were obtained from a Chevenard automatic thermobalance. With this instrument a heating rate of 25 °C/hr was used with approximately 0·5 g of material and the furnace open to the air. The sensitivity was 2·38 mg/mm deflexion on the photographic film. The differential thermal analyses were carried out on automatic equipment described by Carthew and Cole (1953). A heating rate of 10 °C/min was used with 0·3 g of material and the furnace open to the air. With each run a sensitivity of 2·2 μV/mm deflexion of the recording pen was used.

The dehydration curves obtained from the Chevenard balance were analysed after plotting the first derivative graphically in a manner analogous to that used by de Keyser (1953) in his automatic differential thermobalance. This method gave a standard procedure for fixing the composition of phases that were represented only by changes of slope in the weight-loss curve. The differential weight-loss curves for the oxychlorides differ little from the differential thermal curves, indicating the accuracy of the plotting technique.

III. Thermal Dehydration to the Anhydrous Phases

(*a*) *Low Temperature Forms*

(i) *3-Form.*—Feitknecht and Held (1944) showed by isobaric dehydration combined with X-ray examination that $3Mg(OH)_2.MgCl_2.7H_2O$ has two lower hydrates with 5 and 3 molecules of water and an anhydrous phase. The stable temperature of these lower hydrates was 30 and 65 °C, respectively. The anhydrous phase which had the same structure as $Mg(OH)_2$ was stable at a temperature of 180 °C. Wehner (1953) has recently published results that were in agreement with those of Feitknecht and Held. However, Feitknecht (1953) has also recently published new data, communicated to him by de Wolff, in which he accepts 8, 6, 4, and 0 as being the correct numbers of water molecules for the 3-form and its dehydration phases. These compositions are then capable of a structural interpretation. The present results (discussed in more detail below) agree with the existence of the hydrate with 4 molecules of water but not that with 6 ; it is considered that the correct numbers of water molecules for the 3-form and its dehydration phases are 8, 5, 4, and 0. Bianco (1951) has noted the existence of a monohydrate of the 3-form prepared in solution at a temperature above 100 °C, but de Wolff, Walter-Lévy, and Bianco (1953), and

de Wolff and Kortlandt (1954) now consider this material to be anhydrous with a crystal structure of the atacamite type.

The results of the present investigation show that the 3-form has, under natural conditions, 8 molecules of water as established by de Wolff and Walter-Lévy (1949) However, the 8 molecules are readily reduced to 7 by washing with ethanol or by mild heat treatment. The loss in water is accompanied by small changes in the X-ray pattern similar to those illustrated by Wehner (1953). However, isobaric dehydration of the 3-form with 8 molecules of water (Fig. 1 and Table 1) yields lower hydrates with 5 and 4 water molecules and an anhydrous phase but there is no break in the weight-loss curve at 7 molecules of water. Since these results differ from those of earlier workers, a number of different

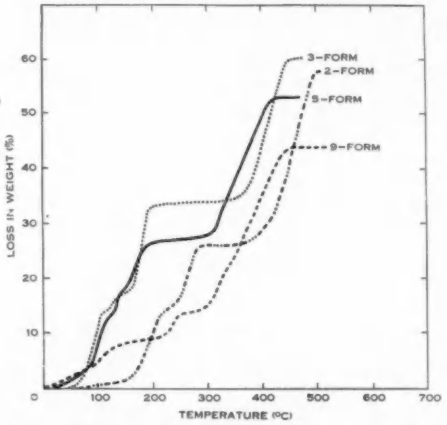


Fig. 1.—Dehydration curves of magnesium oxychlorides as determined on a Chevenard automatic thermobalance. 5-Form, $5Mg(OH)_2.MgCl_2.7.93H_2O$; 3-form, $3Mg(OH)_2.MgCl_2.7.68H_2O$; 2-form, $2Mg(OH)_2.MgCl_2.4.14H_2O$; 9-form, $9Mg(OH)_2.MgCl_2.5.68H_2O$.

preparations were examined. For 5 samples the average numbers of water molecules for the intermediate hydrates were 4·67 and 3·78, and there was no evidence for phases with 7, 6, or 3 molecules of water. It is considered that the difference between results found here and by Feitknecht and Held (1944) and Wehner (1953) is due to their original materials being slightly impure. The interplanar spacings of pure $3Mg(OH)_2.MgCl_2.8H_2O$ tabulated in Table 2 agree with those published by de Wolff and Walter-Lévy (1953) and both differ from that of Wehner (1953) in not possessing a prominent line at 11·0 kX. A line at about this spacing has been shown by de Wolff and Walter-Lévy (1949) and confirmed by the present authors to be due to magnesium chlorocarbonate, the final decomposition product of most magnesium oxychlorides. No explanation can be offered for the difference between the present results and those of Feitknecht (1953).

TABLE 1

DETAILED ANALYSES OF THE WEIGHT-LOSS CURVES (FIG. 1), THE DIFFERENTIAL PLOT OF THE WEIGHT-LOSS CURVES (D.T.B., FIG. 2), AND THE DIFFERENTIAL THERMAL ANALYSIS CURVES (D.T.A., FIG. 2) OF EACH FORM OF MAGNESIUM OXYCHLORIDE

Type	Original Composition of Each Form	D.T.B. and Weight-Loss Curves					D.T.A. Curve
		Minima				Maxima	Peak
		Wt. Loss (%)	Number of H_2O Molecules		Temp. (°C)	Temp. (°C)	Temp. (°C)
			Lost	Remaining			
Compounds formed in solutions at temperatures below 100 °C	$3{\cdot}00Mg(OH)_2.MgCl_2.7.68H_2O$	13·61	3·08	4·60	110	96	145
		17·21	3·90	3·78	143	123	170
		33·82	7·68	0·00	266	177	220
		(34·89)	(7·90)	(—0·22)	(352)	(348)	(378)
		46·59	10·55	—2·87	410	398	430
		60·05*	†	†	460	425	505
	$5{\cdot}00Mg(OH)_2.MgCl_2.7.93H_2O + 0{\cdot}08Mg(OH)_2$	12·62	3·71	4·22	121	100	157
		17·88	5·25	2·68	152	135	184
		27·00	7·93	0·00	245	173	218
		37·21	10·94	—3·01	350	328	364
		(46·84)	(13·77)	†	(390)	(380)	411
		53·11*	†	†	455	398	478
Compounds formed in solutions at temperatures at and above 100 °C	$2{\cdot}00Mg(OH)_2.MgCl_2.4.14H_2O + 0{\cdot}40Mg(OH)_2$	14·38	2·28	1·86	226	188	245
		26·08	4·14	0·00	320	268	284
		33·46	5·31	—1·17	422	418	462, 486
		57·86*	†	†	503	469	546
	$9{\cdot}00Mg(OH)_2.MgCl_2.5.68H_2O + 0{\cdot}13Mg(OH)_2$	9·26	3·71	1·97	193	102	173
		14·14	5·68	0·00	264	242	292
		22·40	8·98	—3·30	338	316	368
		(28·91)	(11·60)	(—5·92)	(372)	(366)	452
		43·82*	†	†	520	388	481

( ) The figures in parentheses refer to minor minima and maxima that may not be real ; other minor details visible in the D.T.B. curves (Fig. 2), but not considered significant, have been omitted.

* All forms show a slightly higher weight loss, of the order of 0·5 per cent., if heating is continued up to 1000 °C ; the loss is extremely gradual.

† In Table 1, loss of water only is considered and is relative to the anhydrous phases. Where chlorine also is obviously lost the numerical values have not been completed.

The interpretation of the differential thermal curve of the 3-form (Fig. 2) up to the development of the anhydrous phase represented by a plateau from 260 to 360 °C follows simply from the differential plot of the weight-loss curve (D.T.B. curve). The latter (Fig. 2) shows minima in the rate of decomposition at water contents of 5, 4, and 0 molecules of water and corresponding minima occur also in the differential thermal curve but are less resolved. It is to be noted that in the curve of the 3-form the first endothermic peak is complex, there being two closely following reactions, whereas the second is simple ; this

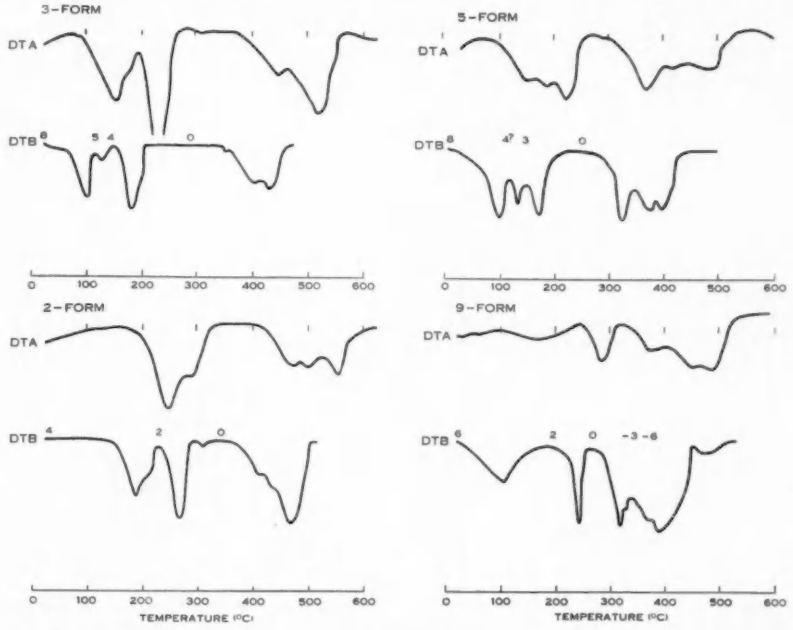


Fig. 2.—Differential thermal analysis curves (D.T.A.) and differential plot of weight-loss curves (D.T.B.) of magnesium oxychlorides. The composition of phases deduced from the latter are indicated above the curves. 5-Form, $5Mg(OH)_2.MgCl_2.7.93H_2O$; 3-form, $3Mg(OH)_2.MgCl_2.7.68H_2O$; 2-form, $2Mg(OH)_2.MgCl_2.4.14H_2O$; 9-form, $9Mg(OH)_2.MgCl_2.5.68H_2O$.

contrasts with the curve of the 5-form, to be discussed later, in which this character of the initial endothermic peaks is reversed. The temperatures of the endothermic reactions from the D.T.A. curve (heating rate 600 °C/hr) are compared in Table 1 with those derived from the D.T.B. curve (heating rate 25 °C/hr) and it can be seen that the former are higher than the latter by about 45 °C. The close correspondence between the D.T.A. and D.T.B. curves for reactions involving loss in weight discussed here has already been pointed out by de Keyser (1953).

TABLE 2

X-RAY DIFFRACTION POWDER PATTERNS OF THE VARIOUS PHASES OF $3Mg(OH)_2.MgCl_2.8H_2O$ AND $5Mg(OH)_2.MgCl_2.8H_2O$ COMPOUNDS FORMED IN SOLUTIONS AT TEMPERATURE BELOW 100 °C THE RESULTS FOR THE 3-FORM (*C* AND *D*) ARE COMPARED WITH THOSE CALCULATED FROM FIGURE 3 OF WERNER (*W*) (1953)

3-Form																5-Form							
$8{\cdot}0H_2O$				$4{\cdot}7H_2O$				$3{\cdot}8H_2O$				$0{\cdot}0H_2O$				$8{\cdot}0H_2O$		$4{\cdot}4H_2O$		$2{\cdot}6H_2O$		$0{\cdot}0H_2O$	
C and *D*		*W**		*C* and *D* 77 °C for 12 Hr		*W* 120 °C for 1 Hr		*C* and *D* 92 °C for 18 Hr		*W*‡ 120 °C for 5 Hr		*C* and *D* 150 °C for 18 Hr		*W* 200 °C for 5 Hr				92 °C for 3 Days		122 °C for 2 Days		148 °C for 2 Days	
I†	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)
		ms	11·03‖	?	11·66‖															vw	11·13		
vs	8·03	s	8·25																	vw	9·62		
w	7·07	mw	7·40					w	7·22	m	7·36					vw	8·15	m	8·66	m	8·55	?	8·49
				mwb	6·69	s	6·73					?	6·70			s	7·57			w	7·84		
mw	5·93	w	5·89	?	6·13			ms	6·21	s	6·07									vw	6·90		
								?	5·47	vw	5·63	s	5·57	s	5·73			ms	6·69	mw	6·42		
								w	5·01	vw	5·04					vw	5·93			vw	5·82		
vw	4·39			mb	4·30	m	4·14	s	4·47	s	4·39									vw	5·35	ms	5·60
mw	4·03	m	4·06							vw	4·09					w	4·90	wb	4·86	w	4·80		
s	3·83	m	3·78	vw	3·86	vw	3·79									w	4·35	s	4·37	m	4·28		
mw	3·53	w	3·59	w	3·62	mw	3·64	w	3·65	w	3·60					ms	4·14						
		vw	3·44	vw	3·40	vw	3·42	vw	3·44	vw	3·42					mw	3·72						
vw	3·24	w	3·25	vw	3·25			?	3·26							vw	3·45						
mw	3·01	m	2·94	mw	3·05	mw	3·06	m	3·07	w	3·03	vw	3·01			mw	3·28	w	3·32	w	3·20		
vw	2·83			vw	2·90	vw	2·82	wd	2·77	vw	2·90	w	2·77	vw	2·82	vw	3·16						
				vw	2·79																		
mw	2·68	m	2·70	mw	2·70	m	2·70	m	2·73	w	2·69					mwb	2·95	mw	2·97	w	2·96		
				m	2·63	ms	2·63	m	2·64	mw	2·60					vvw	2·81	vw	2·83	vw	2·79		
mwd	2·55	m	2·62													w	2·73					w	2·75
								ms	2·495	m	2·472	s	2·487	s	2·501	m	2·64	ms	2·64	mw	2·63		
ms	2·431	ms	2·446	mw	2·465	s	2·465									vw	2·57			vw	2·52		
				mw	2·408	mw	2·402	m	2·414	mw	2·398					vvw	2·495	vw	2·477			md	2·444
vw	2·316			Edge	2·349			w	2·328					vw	2·358	s	2·420	ms	2·412				
w	2·228	w	2·230					vw	2·242	vw	2·228									m	2·385		
vw	2·147	w	2·104	vw	2·185	w	2·193	vwd	2·174	w	2·162							ms	2·357				
				vw	2·116	w	2·103																
w	2·090	vw	2·039	vw	2·054	w	2·050	mw	2·038	w	2·018					mw	2·270			vw	2·206	?	2·260
ms	1·985	m	1·961	mw	1·969	mw	1·966	mw	1·995	w	1·964	mw	1·970	w	1·970	mw	2·204	w	2·223	vw	2·188		
mw	1·937	w	1·900	Edge	1·893	mw	1·915	mw	1·932	w	1·919					vvw	2·155	vw	2·104	vw	2·113		

TABLE 2 (*Continued*)

3-Form																5-Form							
8·0H₂O				4·7H₂O				3·8H₂O				0·0H₂O				8·0H₂O		4·4H₂O		2·6H₂O		0·0H₂O	
C and *D*		*W*•		*C* and *D* 77 °C for 12 Hr		*W* 120 °C for 1 Hr		*C* and *D* 92 °C for 18 Hr		*W*‡ 120 °C for 5 Hr		*C* and *D* 150 °C for 18 Hr		*W* 200 °C for 5 Hr				92 °C for 3 Days		122 °C for 2 Days		148 °C for 2 Days	
I†	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)
mw	1·862	mw	1·842					w	1·883	vw	1·863	vw	1·868			w	2·073	w	{2·015				
w	1·794			vw	1·794			vwd	1·799			vw	1·793			ms	1·978	mw	{1·981	mw	1·986		
				wd	1·767	vw	1·744																
mw	1·724	mw	1·685			w	1·693	wd	1·709							w	1·930					w	1·930
		mw	1·626	vw	1·640	vw	1·665	w	1·647	mw	1·673					vw	1·900	vw	1·884	vw	1·911		
vw	1·618	vw	1·612	vw	1·592	vw	1·586	vw	1·590	vw	1·621	ms	1·610	w	1·590	mw	1·845	w	1·859	vw	1·852	w	1·848
mw	1·588	w	1·525	mw	1·565	vw	1·551	m	1·568	mw	1·550					w	1·781			vw	1·793	vw	1·774
mw	1·543							vw	1·543	vw	1·521	w	1·548	w	1·541	vw	1·750	w	1·724				
				w	1·485			wd	1·492			?	1·475			w	1·709			w	1·699	vw	1·695
mw	1·460	vw	1·405	w	1·428	mw	1·411	wd	1·430							vw	1·681	?	1·686				
				vw	1·396			vwd	1·401	w	1·411	?	1·415			w	1·644	w	1·652				
				vw	1·376					vw	1·378					vw	1·604	w	1·620	w	1·629		
vw	1·345	w	1·343	w	1·355	w	1·350	wd	1·364	m	1·341	w	1·353	vw	1·350	mw	1·581	m	1·573	mw	1·579	m	1·593
								vw	1·306	vw	1·280					mw	1·539	mw	1·548	vw	1·543	w	1·539
		vw	1·251			vw	1·265	vw	1·247			wd	1·252	vw	1·244	w	1·521						
										vw	1·224							wd	1·509	w	1·513	?	1·492
				w	1·202	w	1·202	w	1·208	vw	1·190					vw	1·480			vw	1·480		
w	1·194	vw	1·195													mw	1·452	wd	1·444	w	1·444		
vw	1·180			vw	1·163					vw	1·111					w	1·422					vw	1·426
																w	1·400						
										vw	1·042	w	1·033	vw	1·032					vw	1·385	vw	1·381
										vw	1·010					w	1·365						
																w	1·348					vw	1·340

• The number of water molecules given by Wehner is 10.

† Intensity scale: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak; ?, presence uncertain; d, diffuse; b, broad.

‡ The number of water molecules given by Wehner is 3·1.

|| This line is probably due to magnesium chlorocarbonate.

The existence of lower hydrates of the 3-form is confirmed also by X-ray examination of samples prepared under all heating conditions used in the investigation. Material of composition $3Mg(OH)_2.MgCl_2.8H_2O$ after losing one molecule of water gives an X-ray pattern with small changes in spacings and intensities of a number of lines in the regions 8–6kX, 4·3–3·8 kX, and 2·63–2·40 kX. In particular the line at 7·07 kX increases in intensity, the lines at 8·03 and 5·93 kX are reduced in intensity and new ones appear at 2·61 and 2·406 kX. As the water content is further reduced these changes become more marked and at a composition of $5H_2O$ the lines at 8·03 and 5·93 kX have disappeared leaving the 6·69 kX line as the only prominent one in this region ; in addition the line at 3·83 kX in the original material is greatly reduced in intensity. In contrast to these gradual changes in the X-ray patterns as the material is dehydrated down to $5H_2O$, the subsequent changes to $4H_2O$, and the anhydrous phase are sharp and more typical of true phase transformations. The detailed X-ray patterns of the 3-form and its lower hydrates are compared in Table 2 with those published by Wehner (1953).

(ii) *5-Form.*—The only previous dehydration data for the 5-form is that published by Feitknecht and Held (1944) who concluded that it, like the 3-form, contained 7 molecules of water and had two lower hydrates with 5 and 3 water molecules, and an anhydrous phase. The stable temperature of these lower hydrates was 30 and 50 °C, respectively. The anhydrous phase which had the same structure as $Mg(OH)_2$ was stable at a temperature of 180 °C. Like the 3-form, however, the number of water molecules held by the 5-form under natural conditions is now considered to be 8 (de Wolff and Walter-Lévy 1949 ; Feitknecht 1953).

The results of the present investigation have not been decisive in fixing the compositions of the two lower hydrates which exist between the initial material with 7 or 8 molecules of water and the anhydrous phase. Materials showing either 7 or 8 molecules of water initially have the same X-ray diffraction pattern and have similar dehydration curves. The average water contents for the lower hydrates of five samples was 4·32 and 2·63. The difference of 1·69 molecules suggests that the true difference is 2 molecules and since the method of analysis tends to give low values it is possible that the low hydrates contain 5 and 3 molecules of water as found by Feitknecht and Held (1944). The other alternative is 4 and 3 obtained by taking the nearest whole numbers to the analytical figures, and the X-ray diffraction results discussed later suggest that these values could be the correct ones. The dehydration curve for a sample containing 8 molecules of water is presented in Figure 1 and analysed in Table 1.

As in the 3-form the interpretation of the differential thermal curve of the 5-form up to the development of the anhydrous phase follows simply from the differential plot of the weight-loss curve (Fig. 2). It is to be noted that the first endothermic peak is simple, whereas the second is complex (in the example cited in Fig. 2 the three endothermic peaks are resolved but in general the second two are not) thus differing in this respect from the curve of the 3-form. The temperatures of the endothermic peaks of the D.T.A. curves are on the average 50 °C higher than those derived from the D.T.B. curves (Table 1).

The X-ray powder patterns of the 5-form and its lower hydrates are shown in Table 2. The transformation to the phase with 5 or 4 (?) molecules of water is sharp and results in the formation of a structure different from the original, but very similar to that of the 3-form with $4H_2O$. The further transformation of this phase to one with 3 molecules of water involves only slight structural change and appears to be gradual. The main changes in the X-ray patterns lie in the reversal of intensity of the first two prominent lines at about 8·6 and 6·6 kX, improved definition of a line at 4·8 kX, and the replacement of doublets at about 2·38 and 1·99 kX by single lines. The transformation of this phase to the anhydrous one is sharp.

(*b*) *High Temperature Forms*

Oxychlorides of composition $2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ and $9Mg(OH)_2.MgCl_2.5H_2O$, formed in solutions at temperatures above 100 °C, were first described by Walter-Lévy and Bianco (1951) and are discussed by Demediuk, Cole, and Hueber (1955). The X-ray diffraction patterns of both compounds examined in the present study have more high spacings than listed by Walter-Lévy and Bianco (Table 3) and thus indicate that their X-ray camera was not capable of recording spacings greater than 8 kX. The line at 11·5 kX in the pattern of the 9-form is characteristic of it and is not to be confused with one at 11·3 kX shown later in this work to be due to the transformation of oxychlorides to chlorocarbonate.

The dehydration curves of both the 2- and 9-forms (Fig. 1) show that each has a lower hydrate with 2 molecules of water in addition to an anhydrous phase with the same essential crystal structure as the anhydrous phases of the 5- and 3-forms. Details of the dehydration data are given in Table 1, and the characteristic X-ray patterns of all phases of both compounds are set out in Table 3. The X-ray pattern of $2Mg(OH)_2.MgCl_2.2H_2O$ is compared with that published by Bianco (1951) for a compound of the same composition formed in solution under various conditions of concentration from 75 to 100 °C. It is clear that the pattern published by Bianco is due to a mixture of $2Mg(OH)_2.MgCl_2.4H_2O$ and $2Mg(OH)_2.MgCl_2.2H_2O$.

The interpretation of the differential thermal curves of the 2- and 9-forms up to the development of the anhydrous phase follows simply from the differential plot of the weight-loss curves (Fig. 2). The temperatures of the endothermic peaks are compared in Table 1, those from the D.T.A. curves being on the average 50 °C higher than those from the D.T.B. plots.

IV. The Decomposition of the Anhydrous Phases

All forms of oxychloride upon heat treatment dehydrate to anhydrous phases having the crystal structure of $Mg(OH)_2$ in which Cl ions replace (OH) ions to an extent determined by the composition of the original form. The anhydrous phases are represented by an extended plateau in the weight-loss curves (Fig. 1) and in the D.T.A. and D.T.B. curves of Figure 2. Beyond this plateau the anhydrous phases decompose and since they all have the same structure it is to be expected that this decomposition would be essentially the same for all forms.

TABLE 3

X-RAY DIFFRACTION POWDER PATTERNS OF THE VARIOUS PHASES OF $2Mg(OH)_2.MgCl_2.4H_2O$ AND $9Mg(OH)_2.MgCl_2.5H_2O$ COMPOUNDS FORMED IN SOLUTIONS AT TEMPERATURES AT AND ABOVE 100 °C. THE RESULTS ARE COMPARED WITH THOSE PUBLISHED BY WALTER-LÉVY AND BIANCO (1951) AND BIANCO (1951)

2-Form										9-Form							
$4H_2O$				$2H_2O$				$0H_2O$		$5H_2O$				$2H_2O$		$0H_2O$*	
Present Work		Walter-Lévy and Bianco (1951)		Present Work 153 °C for 2 Days		Bianco (1951) (see text)		204 °C for 2 Days		Present Work		Walter-Lévy and Bianco (1951)		204 °C for 2 Days		255 °C for 4 Hr	
I†	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)
s	10·26									mw	11·46			mw	11·31	?	11·46
vw	8·72			wb	7·84	vw	7·90			vw	9·39						
m	7·46	m	7·43			vw	7·46			s	7·96	s	7·88	m	7·96	vw	8·10
vw	6·65									m	7·30	m	7·14	mw	7·12	vw	7·07
vw	6·17							vw	6·18	vw	6·50			vw	6·50		
ms	5·55	vs	5·51	ms	5·48	vs	5·36	s	5·63	mw	5·82	w	5·86	wd	5·67	s	5·46
vw	5·21									vvw	5·24						
w	4·78							vwd	4·56	vvw	4·52					w	4·76
vwb	4·28									ms	4·07	s	4·04	w	4·20		
ms	3·89	s	3·86			vw	3·96							vw	4·00		
vw	3·72					vw	3·76			m	3·64	m	3·62	w	3·57		
				w	3·55	vw	3·58			vw	3·42						
mw	3·40	w	3·37	vw	3·42	m	3·46			vw	3·32						
mw	3·29	w	3·25			w	3·34			w	3·06	vw	3·05	w	2·98		
w	3·11			wb	3·17					vw	2·77	vvw	2·76	w	2·77	w	2·72
ms	2·94	w	2·92	m	2·94	w	2·88			mw	2·65	w	2·62	vw	2·68		
w	2·78	w	2·74	w	2·74			wd	2·79	vw	2·490			m	2·477		
w	2·72					m	2·68			ms	2·400	s	2·394	w	2·394	s	2·425
m	2·61	m	2·58	w	2·60									vw	2·305	w	2·345
vw	2·522	mw	2·488	s	2·517	w	2·531			m	2·260	s	2·252	mw	2·239		
ms	2·426	s	2·408			s	2·427			vw	2·137	w	2·135	vwd	2·109		
w	2·357	vw	2·330	vw	2·285					vw	2·054						
				vw	2·145	vw	2·206			m	1·977	m	1·969	wd	1·961		
w	2·068	vvw	2·047	mw	2·040	m	2·008	mw	1·994	wd	1·877			w	1·877	mwb	1·910
				w	1·957											?	1·834
mwd	1·945	m	1·925	w	1·914									vw	1·810	w	1·790

TABLE 3 (*Continued*)

2-Form										9-Form							
$4H_2O$				$2H_2O$				$0H_2O$		$5H_2O$				$2H_2O$		$0H_2O$*	
Present Work		Walter-Lévy and Bianco (1951)		Present Work 153 °C for 2 Days		Bianco (1951) (see text)		204 °C for 2 Days		Present Work		Walter-Lévy and Bianco (1951)		204 °C for 2 Days		255 °C for 4 Hr	
I†	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)	*I*	*d* (kX)
mw	1·891	w	1·873			w	1·887	vw	1·870							vw	1·743
mw	1·855	w	1·840			vw	1·851			mwb	1·706	w	1·691	vw	1·686	vw	1·678
						vw	1·817	vw	1·810	m	1·588	w	1·585	mw	1·598	vw	1·623
wd	1·772	vw	1·746	wd	1·737	vw	1·731			vw	1·562	vw	1·560	vw	1·570	ms	1·575
vwd	1·688	vvw	1·677			vvw	1·709			m	1·520	m	1·517	w	1·530	mw	1·516
?	1·620					w	1·632	m	1·631	vw	1·490			vw	1·473		
w	1·605	w	1·599	mw	1·608	w	1·609			w	1·452	w	1·454				
mw	1·586	w	1·571	vw	1·578	w	1·590	mw	1·570	vw	1·428			?	1·405		
w	1·508			w	1·525	w	1·549			vwd	1·362			w	1·345	vw	1·371
wd	1·468	vw	1·463	vw	1·460	w	1·498	vw	1·462	w	1·315	vw	1·308			mw	1·326
	1·452	vw	1·441							w	1·287	vw	1·285	w	1·290		
mw	1·390	vw	1·390	vw	1·390	vvw	1·395			vw	1·252					?	1·249
w	1·376	vvw	1·370			vvw	1·370	mw	1·372	vvw	1·239			vwd	1·236		
wd	1·350	vvw	1·339	vw	1·346	vvw	1·349			w	1·215					wd	1·215
						vvw	1·329							vwd	1·190		
w	1·297	vvw	1·291													mw	1·016
vw	1·314															vwd	0·965
vw	1·268															vw	0·913
mw	1·258	vvw	1·256					vwd	1·258							w	0·898
w	1·208	vvw	1·207														
w	1·158	vvw	1·156														
m	1·145																

* This phase may still contain a small amount of the one with 2 molecules of water.

† See footnote Table 2 for intensity scale.

In the decomposition of the anhydrous phases of the 2-, 5-, and 9-forms during D.T.A., three endothermic reactions, which vary considerably in position and intensity from form to form (Fig. 2 and Table 1), apparently take place. For the 3-form there are only two distinct endothermic peaks in the same region of the D.T.A. curve, although inflexions occur at lower and higher temperatures. X-ray examination of the product after reactions represented by the completion of each endothermic peak shows that as the amount of the anhydrous phase decreases so the MgO content increases. Throughout the decomposition hydrogen chloride is liberated rather than chlorine. These results suggest that the decomposition of the anhydrous phases takes place endothermically by loss of water and chlorine and is accompanied by exothermic reactions between the by-products. Thus

$$n\mathrm{Mg(OH)_2.MgCl_2}$$

$$\downarrow \text{ Endothermic}$$

$$n\mathrm{MgO} + (n-1)\mathrm{H_2O} + \mathrm{H_2O} + \mathrm{MgCl_2}$$

$$\downarrow \text{ Endothermic followed by exothermic}$$

$$\mathrm{MgO} + 2\mathrm{HCl},$$

(where n can be 2, 3, 5, or 9) and the three " apparent " endothermic peaks arise from these interacting reactions.

Detailed examination of the weight-loss curves of the 5- and 9-forms (Fig. 1) shows that each has an inflexion following the commencement of the decomposition of the anhydrous phase and in the plot of the differential of the weight-loss curve (Fig. 2) there is a corresponding deep minimum followed by a strong maximum ; these are not found in the curves of the 2- and 3-forms. For the 5-form with 8 molecules of water originally the maximum corresponds to a loss of 3 molecules of water from the anhydrous phase suggesting that the (OH) content has been reduced to the anhydrous phase of the 2-form, namely,

$$5\mathrm{Mg(OH)_2.MgCl_2} \rightarrow 2\mathrm{Mg(OH)_2.MgCl_2} + 3\mathrm{H_2O} + 3\mathrm{MgO}.$$

X-ray powder photographs show that the volume of the unit cell of the anhydrous phase increases with this dehydration, as expected, and MgO develops. The subsequent decomposition of the anhydrous phase of the 2-form would be as outlined above. The 5-form with 7 molecules of water behaves differently and dehydrates to the anhydrous phase of the 3-form. For the 9-form the maximum corresponds to a loss of 3 molecules of water from the anhydrous phase and a second subsidiary maximum to the loss of 6, but although the latter would correspond to the anhydrous phase of the 3-form, X-ray evidence does not show this to be so. However, it is clear that the anhydrous phases of both the 5- and 9-forms dehydrate by losing (OH) groups before decomposing.

V. The Crystal Structures of the Hydrous Phases

The crystal structure of $3\mathrm{Mg(OH)_2.MgCl_2.8H_2O}$ has been determined by de Wolff and Walter-Lévy (1953) as consisting of puckered layers of infinite double chains of $\mathrm{MgO_6}$ octahedra parallel to (100) and extending in the b-direction. Both (OH) ions and $\mathrm{H_2O}$ molecules provide the oxygen atoms which form the

corners of the octahedra and other H_2O molecules alternate with an equal number of chlorine ions to form rows parallel to *b* between the layers. The structure can be written symbolically as

$$[Mg_4(OH)_6(H_2O)_6 \quad (\overset{\cdots\cdots\cdots}{\underset{\cdots\cdots\cdots}{\longrightarrow}} \quad Cl_2(H_2O)_2]$$

(Feitknecht 1953). Feitknecht considers the dehydration as taking place in stages from 8→6→4 molecules of water by 2 water molecules being lost simultaneously, 1 from the interlayer position and 1 from the edge of the layer, followed by a readjustment of a chlorine position to balance the charge. Thus for the first stage

$$[Mg_4(OH)_6(H_2O)_6 \quad (\overset{\cdots\cdots\cdots}{\underset{\cdots\cdots\cdots}{\longrightarrow}} \quad Cl_2(H_2O)_2] \rightarrow [Mg_4(OH)_6Cl(H_2O)_5$$

$$(\overset{\cdots\cdots\cdots}{\underset{\cdots\cdots\cdots}{\longrightarrow}} \quad ClH_2O] + 2H_2O$$

and for the second stage

$$[Mg_4(OH)_6Cl(H_2O)_5 \quad (\overset{\cdots\cdots\cdots}{\underset{\cdots\cdots\cdots}{\longrightarrow}} \quad ClH_2O] \rightarrow 2[Mg_2(OH)_3Cl(H_2O)_2] + 2H_2O.$$

These reactions imply that the bonding of each chlorine atom and water molecule group between the layers is different but in the structure proposed by de Wolff and Walter-Lévy this cannot be so; either the structure is more complex or the dehydration simpler than that proposed by Feitknecht (1953). The results of the present work show that the 3-form has dehydration phases with 5, 4, and 0 molecules of water rather than 6, 4, and 0, consequently the theory postulated by Feitknecht for dehydration to the phase with $4H_2O$ cannot hold and the structure must be more complex than that proposed by de Wolff and Walter-Lévy. The dehydration of the phase with $4H_2O$ to the anhydrous phase takes place in a single stage as discussed by Feitknecht (1953).

The crystal structure of $5Mg(OH)_2.MgCl_2.8H_2O$ has been represented symbolically, by analogy with the 3-form, as

$$[Mg_6(OH)_{10}(H_2O)_6 \quad (\overset{\cdots\cdots\cdots}{\underset{\cdots\cdots\cdots}{\longrightarrow}} \quad Cl_2(H_2O)_2]$$

(Feitknecht 1953). It is thus to be expected that, like the 3-form, it will dehydrate to a phase with 4 molecules of water. However, in the present work, there is some uncertainty as to whether the phases observed possess 5 and 3 or 4 and 3 molecules of water, but the structure of the first dehydration phase is similar to that of $3Mg(OH)_2.MgCl_2.4H_2O$ suggesting that it too has 4 molecules of water. It dehydrates to a phase with 3 molecules of water with only a small change in structure before passing to the anhydrous phase, thus behaving differently from the 3-form. It is clear that the dehydrations of the 3- and 5-forms differ owing to initial differences in structure, and caution must be exercised in drawing analogies between them.

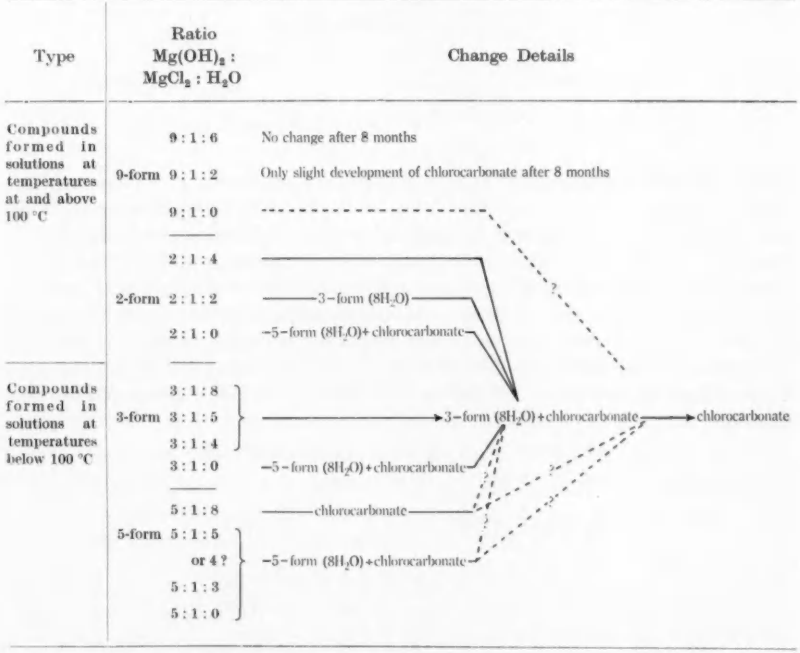
As yet too little is known about the crystal structures of the 2- and 9-forms to permit a discussion here of the structural relationships of the various phases.

VI. The Crystal Structures of the Anhydrous Phases

Feitknecht and Held (1944) have shown that the anhydrous phases $3Mg(OH)_2.MgCl_2$, and $5Mg(OH)_2.MgCl_2$ have the same structure as $Mg(OH)_2$ and that the volumes of their unit cells when plotted against the $Mg(OH)_2 : MgCl_2$ ratio lie on a straight line joining the volumes of the unit cells of $Mg(OH)_2$ and $MgCl_2$. For the present data, calculation of the volumes of the unit cell from Tables 2 and 3 (based on the lines at approx. 5·60 and 1·60 kX being, respectively (001) and (110) of a hexagonal cell) show that for the anhydrous phases of the

Table 4

DIAGRAMMATIC REPRESENTATION OF THE CRYSTALLINE CHANGES UNDERGONE BY MAGNESIUM OXYCHLORIDES AND THEIR HIGH TEMPERATURE PHASES UPON EXPOSURE TO AIR OVER A PROLONGED PERIOD


Type
Ratio Mg(OH)2 : MgCl2 : H2O
Change Details
Compounds formed in solutions at temperatures at and above 100 °C
9-form
2-form
Compounds formed in solutions at temperatures below 100 °C
3-form
5-form
9 : 1 : 6
9 : 1 : 2
9 : 1 : 0
2 : 1 : 4
2 : 1 : 2
2 : 1 : 0
3 : 1 : 8
3 : 1 : 5
3 : 1 : 4
3 : 1 : 0
5 : 1 : 8
5 : 1 : 5 or 4 ?
5 : 1 : 3
5 : 1 : 0
No change after 8 months
Only slight development of chlorocarbonate after 8 months
3-form (8H2O)
5-form (8H2O) + chlorocarbonate
3-form (8H2O) + chlorocarbonate
chlorocarbonate
?

2-, 3-, 5-, and 9-forms the volumes are 51·9, 50·0, 49·2, and 46·9 kX[3], respectively. The chemical formula of the anhydrous phases can be reduced (in the same order) to $Mg(OH)_{1\cdot33}Cl_{0\cdot67}$, $Mg(OH)_{1\cdot50}Cl_{0\cdot50}$, $Mg(OH)_{1\cdot67}Cl_{0\cdot33}$, and $Mg(OH)_{1\cdot80}Cl_{0\cdot20}$ showing the similarity to the $Mg(OH)_2$ structure and the reduction in cell volume with increasing (OH) groups according to the relationship first established by Feitknecht and Held. The (OH) and Cl ions are statistically distributed about the anion space (Feitknecht and Held 1944). It is to be noted here that the anhydrous phase of the 3-form recently described by de Wolff, Walter-Lévy,

and Bianco (1953) is a β-form with the atacamite structure, and is not to be confused with the α-form first proposed by Feitknecht and Held and discussed here.

VII. Stability of Phases

Once the identity of each high temperature phase had been established, its stability was investigated by exposing it to air for a long period. To do this samples of all phases of each form were placed in small thin-walled silica tubes and X-rayed at frequent intervals over a period of 8 months. These experiments which helped to interpret some of the preparations formed in the earlier work of Demediuk, Cole, and Hueber (1955) have confirmed the findings of Walter-Lévy and de Wolff (1949) and Walter-Lévy and Bianco (1951) on the characteristic breakdown in air of the 2-, 3-, and 5-forms to magnesium chlorocarbonate and of the stability of the 9-form, and have supplied new information on the behaviour of the high temperature phases of each form.

The effect of exposure to the atmosphere up to a period of 8 months is shown diagrammatically in Table 4 for all forms. The anhydrous phases of the 2- and 3-forms hydrate first to form $5Mg(OH)_2.MgCl_2.8H_2O$, together with some magnesium chlorocarbonate. The 5-form then transforms into $3Mg(OH)_2.MgCl_2.8H_2O$ with an increase in chlorocarbonate. With continued exposure to air the 3-form gradually changes completely to chlorocarbonate. Hydrated phases usually transform directly into $3Mg(OH)_2.MgCl_2.8H_2O$ without passing through any detectable phase of the 5-form before forming the chlorocarbonate. In the 5-form, the lower hydrates first re-form $5Mg(OH)_2.MgCl_2.8H_2O$ and then behave in a manner similar to this compound. However, the reactions are slow and it is uncertain yet whether these materials pass through the 3-form in their final stages of carbonation, or proceed direct to the chlorocarbonate. The only phase of the 9-form affected by exposure to air after 8 months has been the anhydrous phase. This transformed into magnesium chlorocarbonate after 3 to 6 months' exposure but the X-ray patterns did not indicate whether it had passed through any intermediate compounds. A further series of experiments is desired with shorter intervals of time between X-ray exposures for the anhydrous phase of both the 5- and 9-forms.

Magnesium chlorocarbonate, the characteristic decomposition product of the magnesium oxychlorides, has the formula $Mg(OH)_2.MgCl_2.2MgCO_3.6H_2O$ and forms from $3Mg(OH)_2.MgCl_2.8H_2O$ by carbonation of two $Mg(OH)_2$ groups. (It has been proved during the investigation that the exclusion of carbon dioxide from samples of all forms prevents the decomposition.) Although de Wolff and Walter-Lévy (1949) give the unit cell dimensions of this chlorocarbonate they do not publish the X-ray powder data of Table 5 which is essential for its identification. It is interesting to note that the X-ray pattern of $MgCO_3.3H_2O$ has many similarities to the chlorocarbonate (see Table 5) indicating that the structure of the latter must be built around the $MgCO_3.3H_2O$ units which it contains.

TABLE 5

X-RAY DIFFRACTION POWDER PATTERN OF MAGNESIUM CHLOROCARBONATE ($Mg(OH)_2.MgCl_2.2MgCO_3.6H_2O$) COMPARED WITH THAT OF HYDRATED MAGNESIUM CARBONATE ($MgCO_3.3H_2O$)

Chlorocarbonate		Carbonate		Chlorocarbonate		Carbonate		Chlorocarbonate		Carbonate	
*I**	*d* (kX)	*I**	*d* (kX)	*I**	*d* (kX)	*I**	*d* (kX)	*I**	*d* (kX)	*I**	*d* (kX)
vvs	11·56			w	2·438	mw	2·51	w	1·607	vw	1·598
vw	9·36			w	2·340	w	2·357	w	1·578	w	1·553
vw	7·84			m	2·233	wb	2·182	w	1·527	w	1·511
m	6·70	m	6·59	w	2·109			w	1·496		
mw	5·83	vw	5·56	m	2·055			w	1·468	w	1·460
vw	5·38			mw	2·032	mw	2·028			w	1·432
vw	4·83	w	5·03	vw	1·952			w	1·420		
m	4·39	vw	4·20	mw	1·922	mw	1·933	w	1·394	w	1·394
w	3·87	m	3·89	w	1·900	vw	1·892	vw	1·372		
vw	3·58	w	3·60	w	1·849			w	1·362		
ms	3·39			w	1·827	vwb	1·834			vw	1·348
ms	3·25	w	3·25	w	1·771	w	1·800	w	1·335		
s	3·01	mw	3·05	w	1·731	w	1·724				
w	2·82	w	2·78	mw	1·695						
ms	2·66	m	2·64	vw	1·650	w	1·650				

* See footnote to Table 2 for intensity scale.

VIII. Acknowledgments

The authors wish to express their thanks to Mr. A. R. Carthew and Mr. D. A. Powell of this Division for making the differential thermal analysis and automatic dehydration curves respectively.

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CHEMICAL CONSTITUTION AND ANTHELMINTIC ACTIVITY

II. PREPARATION OF SOME ANALOGUES OF PHENOTHIAZINE

By J. CYMERMAN-CRAIG,* W. P. ROGERS,† and G. P. WARWICK*

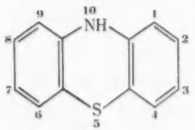
[*Manuscript received November* 17, 1954]

Summary

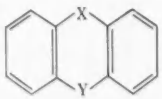
A convenient synthesis of 2,3-dihydrobenzo-1,4-thiazine has been developed, and the preparation of a number of substituted diphenylamines, phenothiazines, and phenoselenazines is described.

I. INTRODUCTION

In Part I of this series (Rogers, Cymerman-Craig, and Warwick, unpublished data), examination of the anthelmintic activities of a series of analogues of phenothiazine (I) was described. These were tricyclic structures of the two types II and III in which X and Y were the various possible combinations of C, N, O, S, and Se. Only phenothiazine (I) and its close analogue phenoxazine (II ; X=NH, Y=O) were found to possess appreciable anthelmintic activity against *Syphacia obvelata* in mice. In view of this result, a number of substituted phenothiazines were prepared to examine the variation of activity with substitution within this series, and the present paper deals with the synthesis of those compounds not previously described.



(I)



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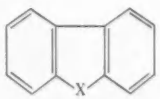

(III)

As a phenothiazine analogue containing only two fused rings, 2,3-dihydrobenzo-1,4-thiazine (IV) was required. Langlet (1896) describes its preparation in poor yield from ethylene dibromide and 2-aminothiophenol. Reduction of 2,2′-dinitrodiphenyl disulphide by the method of Claasz (1912) gave only 2,2′-diaminodiphenyl disulphide, which was not further reduced by hydrogen sulphide but gave on lithium aluminium hydride reduction a 76 per cent. yield of the desired 2-aminothiophenol, also obtainable from 2-mercaptobenzthiazole in 85 per cent. yield by an adaptation of the method of Kiprianov, Ushenko,

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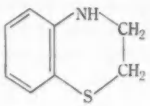
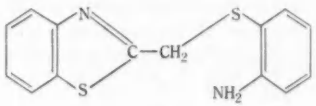
and Gershun (1944). Condensation of 2-aminothiophenol with bromoacetic acid (Unger and Graff 1897) gave 2,3-dihydro-3-ketobenzo-1,4-thiazine; continuous extraction of this with ether showed the presence of 8 per cent. of 2,2′-diaminodiphenyl disulphide (as a hydrobromide), probably formed by oxidation of the thiophenol during condensation with bromoacetic acid. Reduction of the lactam with lithium aluminium hydride afforded IV in excellent yield as a crystalline solid, m.p. 35 °C, characterized as the picrate.

The base $C_{14}H_{12}N_2S_2$ obtained from 2-aminothiophenol and bromoacetyl bromide (Unger and Graff 1897) was prepared and characterized as the alkali-soluble benzenesulphonyl derivative. The formulation of the base as 2-(2′-aminophenylthio)methylbenzthiazole (V) is supported by Kiprianov, Suitnik, and Grigoreva's (1936) preparation of 2-methylbenzthiazole from 2-aminothiophenol and acetic anhydride.



(IV)



(V)

Phenothiazine readily gave the 10-formyl derivative in quantitative yield, previously obtained (Charpentier 1947) only by oxidation of 10-propenylphenothiazine. Reduction of this formyl compound by lithium aluminium hydride, either in ether or tetrahydrofuran solution, gave only phenothiazine; no 10-methylphenothiazine was isolated.

Fusion of diphenylamine-2-carboxylic acid with sulphur at 230 °C was accompanied by decarboxylation giving phenothiazine as sole product; Gilman, Shirley, and Van Ess (1944) isolated only unchanged acid from this reaction at 180 °C. Attempted fusion of 2-nitrodiphenylamine with sulphur failed at both 180 and 230 °C, in the former case unchanged starting material being isolated, while at the higher temperature much decomposition occurred. Attempted removal of oxygen from 3-nitrophenothiazine sulphoxide (Kehrmann and Nossenko 1913) was unsuccessful, but 3-nitrophenothiazine was readily obtained by the excellent method of Evans and Smiles (1935*b*).

4,4′-Dimethyldiphenylamine was converted into its *N*-acetyl and *N*-methyl derivatives, and 4-phenyldiphenylamine prepared by condensation of 4-aminodiphenyl and 2-iodobenzoic acid (no reaction occurred with 2-chlorobenzoic acid), followed by decarboxylation, in 45 per cent. overall yield. This amine has previously been prepared (Piccard 1926) in unstated yield from 4-acetylaminodiphenyl and iodobenzene. Fusion of the amine with sulphur in the presence of iodine (Knoevenagel 1914) gave a quantitative conversion to 3-phenylphenothiazine, and by the same method 3,7-dimethoxyphenothiazine was obtained in 69 per cent. yield from 4,4′-dimethoxydiphenylamine. Fusion of 4,4′-dimethyldiphenylamine with sulphur at 180 °C and then at 245 °C gave 3,7-dimethylphenothiazine previously obtained (Kehrmann 1906) in 2–3 per

cent. yield. A quantitative conversion of 4-methyldiphenylamine to 3-methylphenothiazine was achieved by fusion with sulphur at 180 °C; the temperature (280 °C) reported by Gilman and Shirley (1944) may be a misprint. Fusion of 4-chlorodiphenylamine with sulphur was accompanied by loss of hydrogen chloride, and gave only phenothiazine. Knoevenagel (1914) records that in the fusion of the isomeric *N*-chlorophenylnaphthylamines with sulphur at 180 °C, only the *m*-chloro-compounds gave the expected chlorobenzphenothiazines; *o*- or *p*-chloro-compounds gave evolution of hydrogen chloride and hydrogen sulphide and no product was described. The desired 3-chlorophenothiazine was readily obtained by Evans and Smiles's (1935*b*) method, and the same reaction was employed to prepare the 3-bromo- and 3-iodo-analogues.

Condensation of 2-aminothiophenol and 2,5-dibromonitrobenzene gave 2-nitro-4-bromo-2′-aminodiphenyl sulphide, the acetyl derivative of which underwent the Smiles rearrangement (Evans and Smiles 1935*a*) to give 3-bromophenothiazine in almost quantitative yield. Application of this method to the acetyl derivative of 4-iodo-2-nitro-2′-aminodiphenyl sulphide, obtained from 2-aminothiophenol and 2,5-di-iodonitrobenzene, similarly afforded 3-iodophenothiazine in excellent yield. This compound has not been reported in the chemical literature, but Professor P. Carodemos of Clemson College, South Carolina (personal communication) informs us that he has recently obtained this substance by the Sandmeyer reaction from 3-aminophenothiazine.

Fusion of 4-fluorodiphenylamine with sulphur at 150–155 °C (Smith 1951) gave 3-fluorophenothiazine as described by this author. It was therefore somewhat surprising that fusion of the same reactants at 180 °C yielded only phenothiazine, identified by m.p. and mixed m.p.

Preparation of 3-methylphenoselenazine was carried out by the method of Cornelius (1913) from 4-methyldiphenylamine and selenium monochloride; and 10-methylphenoselenazine, previously obtained by the same author in unstated yield by methylation of phenoselenazine with methyl iodide and methanol under pressure, was readily obtained in 60 per cent. yield using dimethyl sulphate.

II. Experimental

Analyses are by the late Mrs. E. Bielski and Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory.

(*a*) *Reduction of 2,2′-Dinitrodiphenyl Disulphide.*—Reduction of 2,2′-dinitrodiphenyl disulphide by the method of Claasz (1912) gave only 2,2′-diaminodiphenyl disulphide as lemon-yellow plates, m.p. 93 °C (diacetyl derivative, m.p. 163–164 °C). The *dihydrochloride* crystallized from dilute hydrochloric acid as pale cream needles, m.p. 112–114 °C (Found: N, 9·1%. Calc. for $C_{12}H_{12}N_2S_2.2HCl$: N, 8·8%).

(*b*) *2-Aminothiophenol.*—(i) A mixture of 2,2′-diaminodiphenyl disulphide (2·48 g) and lithium aluminium hydride (3·34 g) in ether (350 ml) was refluxed for 12 hr, the mixture made strongly alkaline, and extracted with ether. Removal of solvent from the ethereal extracts gave unchanged amine (0·2 g; 8%). The aqueous layer was brought to pH 7·5 with hydrochloric acid and extracted with ether. Distillation of the dried extracts afforded 2-aminothiophenol (1·9 g; 76%) as a yellow oil, b.p. 125 °C/6 mm.

(ii) 2-Mercaptobenzthiazole (50 g) was hydrolysed with sodium hydroxide solution (55% w/v; 110 ml) in an autoclave at 200 °C for 4 hr (Kiprianov, Ushenko, and Gershun 1944).

On cooling, the light brown filtrate was neutralized to pH 7 and extracted with ether. Distillation of the dried extracts gave 2-aminothiophenol (31·2 g; 85%) as a pale yellow liquid, b.p. 122–125 °C/6 mm. (Kiprianov, Ushenko, and Gershun (1944) give 50% yield.)

(*c*) *2,3-Dihydrobenzo-1,4-thiazine.*—A mixture of 2,3-dihydro-3-ketobenzo-1,4-thiazine (1·3 g, Unger and Graff 1897), lithium aluminium hydride (0·3 g), and ether (350 ml) was refluxed for 5·5 hr. The mixture was allowed to stand overnight and was decomposed by addition of ammonium chloride solution. Sodium hydroxide solution was added and the mixture extracted with ether. Removal of solvent gave an oil (1·18 g, theoretical) which on distillation afforded 2,3-dihydrobenzo-1,4-thiazine (0·9 g; 77%) as a pale yellow viscous oil, b.p. 115–117 °C/0·4 mm, n_D^{14} 1·6651 which solidified on standing, crystallizing from light petroleum (b.p. 60–80 °C) as plates, m.p. 35 °C (Found: N, 9·1; S, 21·0%. Calc. for C_8H_9NS: N, 9·3; S, 21·2%). (Langlet (1896) reports b.p. 265 °C/760 mm). The *picrate* crystallized from aqueous ethanol as lemon-yellow plates, m.p. 139 °C (Found: N, 14·5; S, 8·2%. Calc. for $C_8H_9NS.C_6H_3O_7N_3$: N, 14·8; S, 8·5%).

(*d*) *2-(2′-Aminophenylthio)methylbenzthiazole.*—Prepared from 2-aminothiophenol and bromoacetyl bromide (Unger and Graff 1897) the base had m.p. 89–90 °C (Unger and Graff (1897) report m.p. 88–89 °C); mixed m.p. with 2,2′-diaminodiphenyl disulphide was 72–76 °C (Found: C, 61·4; H, 4·4; N, 10·6%. Calc. for $C_{14}H_{12}N_2S_2$: C, 61·8; H, 4·4; N, 10·3%). The *benzenesulphonyl* derivative, prepared from the amine and benzenesulphonyl chloride in pyridine, was readily soluble in dilute aqueous sodium hydroxide. It separated from benzene-light petroleum (b.p. 60–80 °C) as needles, m.p. 119 °C (Found: N, 6·6%. Calc. for $C_{20}H_{16}O_2N_2S_2$: N, 6·8%).

(*e*) *N-Acetyl-4,4′-dimethyldiphenylamine.*—The *acetyl* derivative crystallized from aqueous methanol as prisms, m.p. 85–86·5 °C (Found: C, 80·7; H, 7·0%. Calc. for $C_{16}H_{17}ON$: C, 80·3; H, 7·2%).

(*f*) *N-Methyl-4,4′-dimethyldiphenylamine.*—A mixture of 4,4′-dimethyldiphenylamine (1·5 g) and methanol (13 ml) was treated with dry hydrogen chloride for 3 min. The yellow solution was sealed in a Pyrex tube and heated at 125–135 °C for 5 hr. After removal of volatile products, the residual heavy oil was distilled *in vacuo* to give the *amine* as a pale yellow oil (80%, 1·17 g), b.p. 127–128 °C/0·5 mm, n_D^{23} 1·5975 (Found: N, 6·6%. Calc. for $C_{15}H_{17}N$: N, 6·7%).

(*g*) *4-Phenyldiphenylamine.*—A mixture of 2-iodobenzoic acid (0·2M; 49·6 g), 4-aminodiphenyl (45 g), potassium carbonate (40 g), and spongy copper (0·1 g) was heated to 170–190 °C for 8 hr. The mixture was warmed for 0·5 hr with concentrated hydrochloric acid, and then treated with excess of sodium hydroxide solution. An insoluble sodium salt crystallized as long colourless needles on cooling. A solution of this salt in hot water was treated with concentrated hydrochloric acid, and the precipitate filtered, washed with cold ethanol, and dried at 90 °C (weight, 34 g). The acid was heated at 170–190 °C for 0·75 hr when evolution of carbon dioxide had ceased, giving the amine (22 g, 45%), b.p. 125 °C/0·1 mm, m.p. 112 °C (Piccard (1926) gives m.p. 112 °C).

(*h*) *3-Phenylphenothiazine.*—A mixture of 4-phenyldiphenylamine (2·76 g), sulphur (resublimed, 0·64 g) and iodine (0·1 g) was heated to 170 °C for 10 min, when the melt solidified. After a further 15 min at 225 °C, the *product* (3·1 g, 100%) had m.p. 217 °C. Recrystallization from ethanol/benzene gave lemon-yellow plates, m.p. 218–219 °C (Found: N, 5·3%. Calc. for $C_{18}H_{13}NS$: N, 5·1%).

(*i*) *3,7-Dimethoxyphenothiazine.*—A mixture of 4,4′-dimethoxydiphenylamine (2·29 g), sulphur (0·64 g), and a crystal of iodine was heated at 180 °C for 45 min and then at 195 °C for 5 min. Crystallization from ethanol gave prisms (1·8 g, 69%) of *product*, m.p. 194–196 °C (Found: C, 65·0; H, 5·2; N, 5·6%. Calc. for $C_{14}H_{13}O_2NS$: C, 64·9; H, 5·1; N, 5·4%).

(*j*) *3,7-Dimethylphenothiazine.*—After a mixture of 4,4′-dimethyldiphenylamine (9·08 g), sulphur (2·56 g), and iodine (0·1 g) had been heated at 180 °C for 15 min, the melt solidified. The temperature was then raised to 245 °C for a further 15 min, and the cooled melt extracted with hot acetic acid. The filtrate on dilution with water gave a brown solid, recrystallized from ethanol to give the product, constant m.p. 218–220 °C (Kehrmann (1906) gives m.p. 219–220 °C).

(*k*) *10-Formylphenothiazine.*—Phenothiazine (5 g) and formic acid (75 ml; 98%) were refluxed for 2·75 hr. Most of the formic acid was then distilled off and the remaining solution poured into ice (20 g); one crystallization of the solid (5·6 g, 100%) from ethanol gave needles, m.p. 143–144·5 °C (Charpentier (1947) gives m.p. 144–145 °C).

(*l*) *Lithium Aluminium Hydride Reduction of 10-Formylphenothiazine.*—A mixture of 10-formylphenothiazine (1·7 g) and lithium aluminium hydride (0·17 g) in ether (200 ml) was refluxed for 20 hr. Decomposition by addition of ammonium chloride solution and sodium hydroxide solution, followed by ether extraction, gave phenothiazine (0·7 g), m.p. and mixed m.p. 181–182 °C, as sole product.

Reaction of *N*-formylphenothiazine and lithium aluminium hydride in tetrahydrofuran similarly afforded only phenothiazine (m.p. and mixed m.p.).

(*m*) *2-Nitro-4-bromo-2′-aminodiphenyl Sulphide.* — Neutralization of 2-aminothiophenol (18·8 g) with alcoholic sodium ethoxide gave the sodium salt which was added to 2,5-dibromonitrobenzene (42 g) in ethanol (200 ml). The solution immediately turned brown. It was refluxed for 4 hr and poured into water (3 l.). The heavy oil which separated, solidified on scratching, and crystallized from ethanol as pale yellow needles of the *sulphide* (35·7 g, 73%), m.p. 134·5 °C (Found: C, 44·7; H, 2·7%. Calc. for $C_{12}H_9O_2N_2SBr$: C, 44·3; H, 2·8%).

Acetylation of the preceding amine (32 g) in pyridine (60 ml) with acetic anhydride (16 ml) on the water-bath for 1·5 hr gave the *acetyl* derivative (34 g, 87%), m.p. 153–154 °C, as yellow needles from ethanol (Found: C, 46·0; H, 3·4; N, 7·8%. Calc. for $C_{14}H_{11}O_3N_2SBr$: C, 45·8; H, 3·0; N, 7·7%).

(*n*) *3-Bromophenothiazine.*—The preceding acetyl derivative (12·3 g) in acetone (150 ml) was treated with sodium hydroxide (1·33 g; 1M) in ethanol (17 ml) and heated at 100 °C for 0·5 hr, when another molar proportion of alcoholic sodium hydroxide was added. After a further 0·5 hr refluxing, the mixture was concentrated to half its volume and poured into water (500 ml). Filtration gave *3-bromophenothiazine* (8·5 g, 98%), m.p. 181·5 °C, crystallizing from ethanol as plates of unchanged m.p. (Found: C, 52·0; H, 2·9; N, 4·9%. Calc. for $C_{12}H_8NSBr$: C, 51·8; H, 2·9; N, 5·0%).

(*o*) *4-Iodo-2-nitro-2′-aminodiphenyl Sulphide.*—A solution of 2,5-di-iodonitrobenzene (16·5 g) in ethanol (125 ml) was heated with the sodium salt of 2-aminothiophenol (from 5·5 g of thiol) and the mixture refluxed for 4 hr. On cooling and addition of water, the *sulphide* (13·6 g, 83%) separated, m.p. 126 °C. It crystallized from ethanol as orange needles, m.p. 127·5 °C (Found: C, 38·9; H, 2·5; S, 8·7%. Calc. for $C_{12}H_9O_2N_2SI$: C, 38·8; H, 2·5; S, 8·6%).

Acetylation of this amine (13·6 g) in pyridine (30 ml) with acetic anhydride (8 ml), as described in Section II (*m*), gave the *acetyl* derivative (15·1 g, 98%), crystallizing from ethanol as yellow needles, m.p. 176–176·5 °C (Found: C, 40·8; H, 2·8; S, 7·7%. Calc. for $C_{14}H_{11}O_3N_2SI$: C, 40·6; H, 2·7; S, 7·8%).

(*p*) *3-Iodophenothiazine.*—The preceding acetyl derivative (10·35 g) in acetone (200 ml) was treated with alcoholic sodium hydroxide (1 g) by the method described in Section II (*n*), affording *3-iodophenothiazine* (7·4 g, 91%), crystallizing from ethanol as pale cream plates, m.p. 205 °C (decomp.) (Found: C, 44·4; H, 2·4%. Calc. for $C_{12}H_8NSI$: C, 44·3; H, 2·5%).

(*q*) *Fusion of Diphenylamine-2-carboxylic Acid with Sulphur.*—Fusion of a mixture of diphenylamine-2-carboxylic acid (8·52 g), sulphur (2·56 g), and iodine (0·1 g) at 230 °C for 0·5 hr was accompanied by frothing. The product (7·8 g) was insoluble in alkali and crystallized from ethanol in plates, m.p. 175–176 °C, undepressed on admixture with phenothiazine.

(*r*) *Fusion of 4-Chlorodiphenylamine with Sulphur.*—A mixture of 4-chlorodiphenylamine, sulphur, and a catalytic amount of iodine was heated at 180 °C for 0·25 hr. Purification of the product in benzene solution on an alumina column gave white prisms, m.p. 168–170 °C identified as phenothiazine by mixed m.p. (mixed m.p. 178–180 °C) and by the acetyl derivative (m.p. and mixed m.p.).

(*s*) *Fusion of 4-Fluorodiphenylamine with Sulphur.*—(i) A mixture of 4-fluorodiphenylamine (2·67 g), sulphur (0·91 g), and iodine (0·1 g) was heated at 180 °C for 0·75 hr. Extraction

with ethanol and vacuum-sublimation of the alcohol-soluble material gave pale yellow plates (0·8 g), m.p. 176–177 °C, undepressed on mixed m.p. with phenothiazine. (ii) Repetition of the fusion at 150–155 °C (Smith 1951) for 1 hr followed by chromatography of the product in benzene on alumina gave 3-fluorophenothiazine as plates, m.p. 176–177 °C, mixed m.p. with phenothiazine 165–167 °C (Smith (1951) gives m.p. 176–177 °C).

(*t*) *3-Methylphenoselenazine.*—An ice-cold solution of 4-methyldiphenylamine (31 g) in benzene (70 ml) was treated over 1 hr gradually with a solution of selenium monochloride (44 g) in benzene (20 ml). The mixture was refluxed for 8 hr, filtered hot, and passed through a column of alumina. The first three fractions afforded *3-methylphenoselenazine* (11·3 g, 26%), m.p. 232 °C (decomp.), as plates from benzene-light petroleum (b.p. 60–80 °C) (Found: N, 4·9, 5·0%. Calc. for $C_{13}H_{11}NSe$: N, 5·4%).

(*u*) *10-Methylphenoselenazine.*—Phenoselenazine (13 g) in acetone (100 ml) was treated with sodium hydroxide (4·2 g) and dimethyl sulphate (13 g) with shaking. After 30 min the acetone was distilled off and the residue extracted with benzene. The washed and dried extracts gave 8·6 g (60%) of product, m.p. 138 °C (Cornelius (1913) gives m.p. 138–139 °C).

III. Acknowledgments

One of us (G.P.W.) gratefully acknowledges the award of an Ian McMaster Scholarship.

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THE PARTIAL DEGRADATION OF RING A OF LANOSTENOL

By R. G. Curtis*† and R. Schoenfeld*

[*Manuscript received October* 26, 1954]

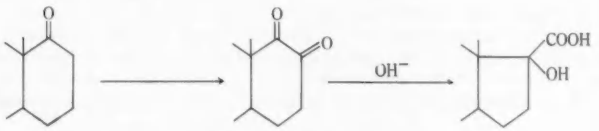
Summary

Bromination of lanostenone (I) followed by alkaline hydrolysis caused contraction of ring A to give an α-hydroxy acid (IV). This compound was subjected to a sequence of reactions terminating in the scission of the contracted ring A.

I. Introduction

Ring contraction has recently been the subject of several interesting studies, for the methods used are of importance in those total syntheses of cortisone in which ring D must be changed from a 6- to a 5-membered ring (see Woodward *et al.* 1952 ; Johnson *et al.* 1953 ; Wieland, Anner, and Miescher 1953).

In this connection the benzilic acid type of rearrangement as applied by Wallach (1918) also seems to deserve attention. Such a reaction, used on D-homosteroid intermediates, would provide, from a ring D ketone, not only ring contraction but also the C_{17} hydroxyl group and the first carbon of the corticosteroid side chain as well :



Wallach employed his technique on monoterpenes. In the steroid group, occurrence of the reaction has occasionally been reported (see Borsche and Frank‡ 1927 ; Woodward and Clifford‡ 1941 ; Fieser and Rajagopalan 1949), but it seems to have been accidental, leading to unwanted products. No attempt to make this reaction the starting point for degradation experiments appears to have been recorded in the literature.

The present paper describes the contraction of ring A of lanostenol (dihydrolanosterol) by a technique similar to that of Wallach. The reaction sequence proceeds smoothly and is apparently stereospecific.

Lanostenol was first oxidized to the ketone I which was then treated with two molecules of bromine to yield the unsaturated bromoketone II. Bromination

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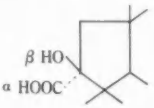
‡ The first two papers cited are in fact reinterpretations of the work of earlier investigators who had failed to recognize the benzilic acid rearrangement.

of the enol acetate of I under identical conditions gave the same compound. Hydrolysis of II with alkali at once gave the hydroxy acid IV in good yield and the probable intermediate III could not be isolated. If IV is the desired product it is also unnecessary to purify II and the conversion of I to IV is much simplified. Careful fractional crystallization of the acid IV, as well as of its methyl ester, acetate, and methyl ester acetate, did not indicate the presence of more than one stereoisomer. A study of molecular models favours the configuration indicated :



The hydroxy acid IV was then used to prepare further derivatives of the A-nor-lanostenol group. Lead tetra-acetate oxidizes IV to the norketone V prepared previously by Ruzicka, Rey, and Muhr (1944) from the dibasic acid X. In this ketone, which now becomes readily accessible, the α-methylene group is however unreactive and the compound is thus not easily made the starting point for further reactions.

The acid IV was therefore dehydrated to the α-unsaturated acid VI which readily decarboxylated to the unsaturated hydrocarbon VII. The action of osmium tetroxide on VII gave an α-glycol VIII. Here again the reaction product appeared to be free from stereoisomers, only one of the two possible *cis*-glycols being isolated.

Oxidative cleavage of the glycol VIII with periodic acid gave the desired dialdehyde (isolated as the dioxime IX), but in poor yield, and the degradative sequence was terminated with this step.

II. Experimental

Melting points were determined in hard glass capillaries and are uncorrected, except where otherwise stated. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(*a*) *Lanost-8-en-3-one* (*I*).—The substance was prepared by the addition of Kiliani solution to lanostenol dissolved in acetone.

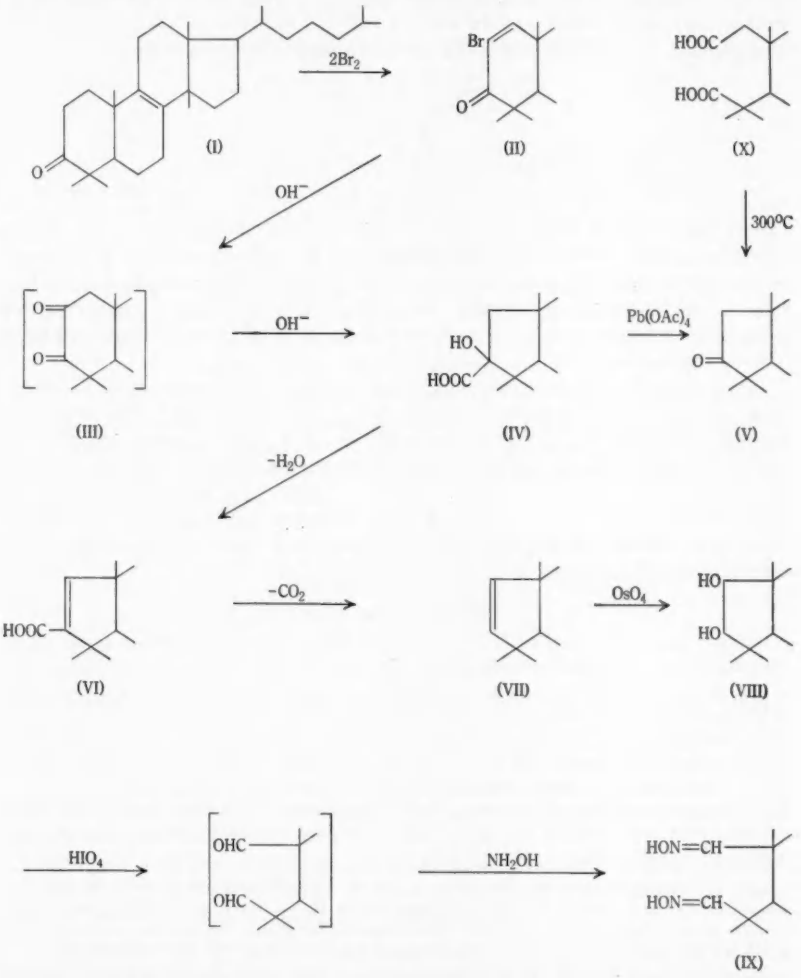
(*b*) *3-Acetoxylanosta-2,8-diene.*—A solution of lanost-8-en-3-one (20 g) in acetyl chloride (40 ml) and acetic anhydride (100 ml) was boiled under reflux (4 hr) and allowed to stand overnight. The crystals, which separated (16 g), were filtered, washed with methanol, and recrystallized successively from ethanol and ethyl acetate. The compound is dimorphous, m.p. 105–107 °C and m.p. 114–115 °C, $[\alpha]_D^{24}$ +125° (*c*, 3 in $CHCl_3$) (Found : C, 82·0 ; H, 10·9%. Calc. for $C_{32}H_{52}O_2$: C, 82·0 ; H, 11·2%).

(*c*) *2-Bromolanosta-1,8-dien-3-one* (*II*).—(i) *From 3-Acetoxylanosta-2,8-diene.* To the enol acetate (2·5 g) and sodium acetate (2 g) dissolved in glacial acetic acid (135 ml) was added bromine (0·6 ml) in acetic acid (20 ml). After standing for 45 min the solution was poured into water and the precipitate crystallized from ethanol to give needles (2 g), m.p. 142 °C, $[\alpha]_D^{24}$ 19·8° (*c*, 3 in $CHCl_3$) (Found : C, 71·6 ; H, 9·5 ; Br, 16·1%. Calc. for $C_{30}H_{47}OBr$: C, 71·6 ; H, 9·4 ; Br, 15·9%).

(ii) *From Lanost-8-en-3-one* (*I*). To the ketone (20 g) in glacial acetic acid (1000 ml) containing a trace of hydrogen bromide, was added a solution of bromine (4·8 ml) in acetic acid (160 ml). After standing overnight crystals had formed, m.p. 142 °C. A mixed melting point determination with material from (i) above showed no depression.

No attempt was made to determine the maximum yield of pure II by this technique, for reasons given in (*d*).

(*d*) *3-Norlanost-8-en-2-ol-2-carboxylic Acid* (*IV*).—This compound IV may be readily obtained from II by refluxing its solution in 20% alcoholic potassium hydroxide. For its



preparation the intermediate II need not be purified, however, and the reaction can be simplified in the following way :

The ketone I was brominated as described above under Section II (*c*) (ii) and the acetic acid solution was poured into cold water. The precipitate was washed with water and heated (1 hr) under reflux in 20% alcoholic potassium hydroxide solution. Water was added and the hydroxy

acid precipitated on acidification of the solution. Crystallization from acetic acid and then from ethyl acetate gave the pure acid in needles melting at 278 °C. Yield of purified material, 10 g, $[\alpha]_D^{24}$ 61·4° (*c*, 3 in $CHCl_3$). Repeated analyses of the acid gave consistently a slightly low value for carbon (Found : C, 78·0 ; H, 11·0 ; O, 10·5%. Calc. for $C_{30}H_{50}O_3$: C, 78·5 ; H, 11·0 ; O, 10·5%). Its identity was therefore confirmed by the preparation of the following derivatives :

(i) *Acetate*, m.p. 207–208 °C (Found : C, 77·0 ; H, 10·5%. Calc. for $C_{32}H_{52}O_4$: C, 76·7 ; H, 10·5%).

(ii) *Methyl ester*, m.p. 114° (Found : C, 78·7 ; H, 11·1%. Calc. for $C_{31}H_{52}O_3$: C, 78·7 ; H, 11·1%).

(iii) *Methyl ester acetate*, m.p. 158 °C (Found : C, 77·3 ; H, 10·3%. Calc. for $C_{33}H_{54}O_4$: C, 77·0 ; H, 10·6%).

(*e*) *(3)-Norlanost-8-ene-2-one (V)*.—The acid IV (1·00 g) was suspended in glacial acetic acid (50 ml) and lead tetra-acetate (2 g) was added. The mixture was swirled occasionally at room temperature. The acid gradually dissolved. After 8 hr, water (10 ml) was added and two-thirds of the solvents distilled off. Ether and water were added to the residue. The washed ether extracts on evaporation gave crystalline material which was taken up in light petroleum and adsorbed on alumina (10 g ; activity I/II). Elution with benzene gave the ketone V in almost quantitative yield. Crystallized from methanol, it melted at 120 °C. A mixed m.p. with material prepared by Ruzicka's (1944) method (m.p. 120 °C ; Ruzicka gives 115 °C) showed no depression.

(*f*) *(3)-Norlanosta-1,8-diene-2-carboxylic Acid (VI)*.—The hydroxy acid IV (5·0 g) was heated in an evacuated tube at 280 °C until evolution of water ceased and the melt solidified. The product, compound VI, was crystallized from methanol : chloroform (1 : 1) and recovered in theoretical yield, m.p. 284 °C (Found : C, 81·8 ; H, 11·0%. Calc. for $C_{30}H_{48}O_2$: C, 81·7 ; H, 11·0%).

Methyl ester, m.p. 146 °C (Found : C, 82·2 ; H, 11·3%. Calc. for $C_{31}H_{50}O_2$: C, 81·9 ; H, 11·1%).

(*g*) *(3)-Norlanosta-1,8-diene (VII)*.—The unsaturated acid VI (3·5 g) was heated (3 hr at 230 °C) in an inert atmosphere with quinoline (35 ml) and copper oxide wire (2 g). Chloroform was added, the solution decanted from the copper oxide, and the quinoline removed with dilute hydrochloric acid. The chloroform solution was washed and the solvent then distilled off. The residue was dissolved in light petroleum and filtered through an alumina column. Crystallization from ethanol gave needles, m.p. 106 °C, yield 1·5 g (Found : C, 88·3 ; H, 12·1%. Calc. for $C_{29}H_{48}$: C, 87·9 ; H, 12·1%).

(*h*) *(3)-Norlanost-8-ene-1,2-diol (VIII)*.—Osmium tetroxide (1 g) was added to a solution of the hydrocarbon VII (1·50 g) in dry ether (50 ml) and pyridine (30 ml) and the mixture was allowed to stand for 6 days. The solvents were then removed under reduced pressure at 40 °C bath temperature. The residue was dissolved in benzene-ethanol (1 : 1 ; 60 ml). Potassium hydroxide (6 g) and mannitol (6 g) in water (15 ml) and ethanol (30 ml) were added, and the mixture refluxed for 6 hr. More benzene was then added and the benzene layer washed several times with water. The benzene was distilled off and the residue was then taken up in light petroleum (b.p. 60–80 °C) and chromatographed on alumina (activity I/II). After the column had been washed with light petroleum and benzene, the diol VIII (1·32 g) was eluted with ethanol-ether (19 : 1). It crystallized from chloroform-methanol as needles, m.p. 143 °C (Found : C, 80·7 ; H, 11·8%. Calc. for $C_{29}H_{50}O_2$: C, 80·9 ; H, 11·7%).

(*i*) *Dioxime (IX)*.—Diol VIII (500 mg) was dissolved in dioxane (25 ml) and periodic acid (250 mg) (determined by titration) in water (6·3 ml) was added. The mixture was left in a refrigerator overnight. Two-thirds of the solvents were removed under reduced pressure at 40 °C. Ether and water were then added, the ether extracts were washed and dried, and the solvent evaporated under reduced pressure. The reaction product remained as a gelatinous mass which could not be made to crystallize.

The dialdehyde was therefore isolated as its dioxime, by refluxing the crude product with a solution of hydroxylamine acetate (prepared from 350 mg $NH_2OH.HCl$) in ethanol (10 ml). After cooling, the solution deposited 180 mg of crystalline material which was recrystallized several times from methanol. The dioxime formed small plates, m.p. 170 °C (Kofler block) (Found : C, 75·9 ; H, 10·6 ; N, 6·3%. Calc. for $C_{20}H_{48}O_2N_2$: C, 76·2 ; H, 10·6 ; N, 6·1%).

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STUDIES ON XANTHORRHOEA RESINS

II. XANTHORRHOEIN AND HYDROXYPAEONOL

By A. J. Birch* and Patricia Hextall*

[*Manuscript received October* 28, 1954]

Summary

The substances, m.p. 80 °C (hydroxypaeonol) and m.p. 68–69 °C (xanthorrhoein) isolated from the resins of several *Xanthorrhoea* spp. by Rennie, Cooke, and Finlayson (1920) are shown to be phloroacetophenone 2,4-dimethyl ether (I ; R=OCH_3) and a (+)-methoxymethylnaphthodihydrofuran probably with one oxygen α- and the other in a β-position of the naphthalene ring.

I. Introduction

As a preliminary step to the investigation of the complex mixture of aromatic compounds found in *Xanthorrhoea* resins we have deemed it advisable to determine the nature of two crystalline compounds isolated by the steam distillation of alkaline solutions by Rennie, Cooke, and Finlayson (1920). We have not been able to isolate these compounds from *X. preissii* Endl. or *X. reflexa* Herbert by any direct fractionation procedure, and the specimens examined were original ones from the University collection.

(*a*) *Hydroxypaeonol*

Rennie, Cooke, and Finlayson (1920) and Finlayson (1926) definitely identified paeonol (2-hydroxy-4-methoxyacetophenone) in the steam distillates of the resins from *X. preissii*, *X. reflexa*, *X. tateana* F. Muell., and *X. arborea* R. Br., together with another phenolic substance, m.p. 80 °C, which they formulated as $C_9H_{10}O_4$ and thought to be 2,6-dihydroxy-4-methoxyacetophenone (I ; R=H) (hydroxypaeonol). This formulation is improbable, because although a 2-acylphenol has a low acidity due to hydrogen bonding the same carbonyl group obviously cannot be simultaneously bonded to two hydroxyl groups, and a substance of such a formula is unlikely to be removed from alkaline solution by steam. The m.p. is close to that of 2-hydroxy-4,6-dimethoxyacetophenone (82 °C) (I ; R=CH_3) and the analysis agrees with the theoretical for $C_{10}H_{12}O_4$ (Found : C, 61·2 ; H, 6·2. Calc. for $C_{10}H_{12}O_4$: C, 61·2 ; H, 6·1%). It differs from the two monomethyl ethers of phloroacetophenone made by Sonn (1928), who suspected it to be a dimethyl ether. An authentic specimen of (I ; R=CH_3) was found to give the same striking colours with nitric acid, an intense blue, converted by heating to blood-red, and to a fugitive dark green on making alkaline. A mixed m.p. confirmed the identity of hydroxypaeonol

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with I (R=CH_3). It may well be an artifact due to alkaline hydrolysis of a chalcone in view of the isolation of 2′,4-dihydroxy-4′-methylchalcone from *X. australis* R. Br. (Duewell 1954, Part I) and of 2′-hydroxy-4,4′-6-trimethoxychalcone from *X. preissii* (Birch and Ryan unpublished data). The co-occurrence of derivatives of phloroacetophenone and resacetophenone is of interest in view of the biosynthetic ideas of Birch and Donovan (1953).

(*b*) *Xanthorrhoein*

The neutral compound, m.p. 68–69 °C, $[\alpha]_D^{13}$ +55·6°, now named xanthorrhoein, was considered by Rennie, Cooke, and Finlayson (1920) to have the formula $C_{13}H_{12}O_2$, which was later amended by Finlayson (1926) to $C_{14}H_{14}O_2$. We have confirmed the latter formulation and have shown the presence of one OCH_3 and one CCH_3. The compound may therefore be formulated as

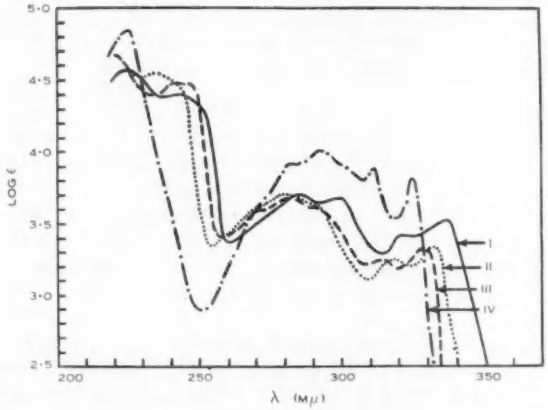
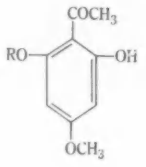


Fig. 1.—Ultraviolet spectra.

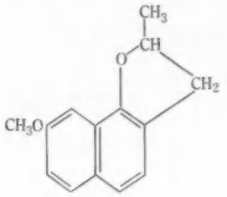
Curve I, xanthorrhoein.
Curve II, 1,7-dimethoxynaphthalene.
Curve III, 1,6-dimethoxynaphthalene.
Curve IV, 1,5-dimethoxynaphthalene.

$C_{12}H_8O(OCH_3)(CH_3)$ and must have an asymmetric centre of some degree of stability in view of the conditions of isolation. Infra-red spectra demonstrate the absence of hydroxyl or carbonyl groups. The substance is very stable to permanganate in acetone and is unaffected by hydrogen in the presence of a palladium-charcoal catalyst. The lack of evidence of unsaturation despite the low proportion of hydrogen, and the formation of an unstable complex with trinitrobenzene indicate the presence of aromatic rings. The ultraviolet absorption spectrum is similar to the spectra of a number of dimethoxynaphthalene derivatives, particularly the 1,6- and 1,7- (Figs. 1 and 2). The presence of another carbon substituent, as in structure II, would probably shift the absorption to slightly longer wavelengths compared with the unsubstituted naphthalene

diether. A formula of the type II would therefore fit all the known facts, although at this stage there is no evidence available to place on the ring the methyl group, which may be in the 2′- or 3′-position, while the ethereal oxygens



(I)



(II)

are probably either 1,6- or 1,7-. We have so far been unable to repeat the isolation of xanthorrhoein from a sample of *X. reflexa* resin kindly supplied by Mr. A. R. Penfold.

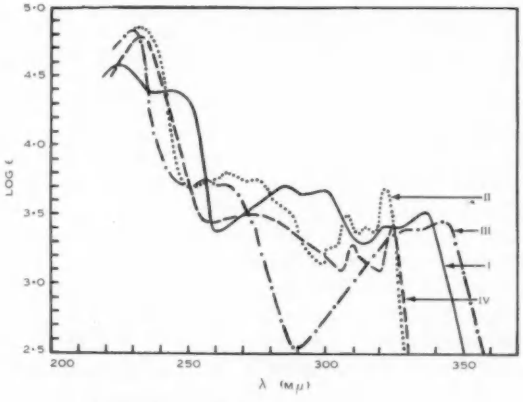


Fig. 2.—Ultraviolet spectra.

Curve I, xanthorrhoein.
Curve II, 2,3-dimethoxynaphthalene.
Curve III, 2,6-dimethoxynaphthalene.
Curve IV, 2,7-dimethoxynaphthalene.

II. Experimental

(*a*) *Xanthorrhoein.*—The specimen was crystallized from ethanol as large colourless prisms, m.p. 69–70 °C, $[\alpha]_D^{16}$ +57·1° (benzene) (Found: C, 78·7; H, 6·6; mol. wt. (Rast), 231; CH_3O, 14·3; CH_3C, 7·1%. Calc. for $C_{14}H_{14}O_2$: C, 78·5; H, 6·5; mol. wt., 214; 1–CH_3O, 14·9; 1–CH_3C, 7·0%). The trinitrobenzene complex formed red needles, m.p. 81 °C.

(*b*) *Ultraviolet Spectra.*—These were determined by a Beckman spectrometer in pure ethanol. The dimethoxynaphthalenes had the following properties: 1,5-, m.p. 181–182 °C; 1,6-, m.p. 59–60 °C; 2,3-, m.p. 117 °C; 2,6-, m.p. 151 °C; 2,7-, m.p. 137–138 °C; 1,7-, oil; picrate, m.p. 132 °C.

III. Acknowledgments

The authors are indebted to the University of Sydney for the award of an Imperial Chemical Industries (A.N.Z.) Fellowship to one of us (P.H.).

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WATER-SOLUBLE CONSTITUENTS OF FRUIT

II. THE SEPARATION OF ACIDS ON ANION-EXCHANGE RESINS : THE ISOLATION OF *l*-QUINIC ACID FROM APRICOTS*

By E. F. L. J. ANET† and T. M. REYNOLDS†

[*Manuscript received December* 13, 1954]

Summary

Displacement chromatography on columns of strongly basic anion-exchange resins has been used to separate, isolate, and purify some water-soluble organic acids. The order of emergence of 27 acids from these columns is recorded. Using this method pure *l*-quinic, succinic, L-malic, and citric acids were isolated from the flesh of the apricot fruit. The method was also used for the purification of hydroxy-acids.

The detection of acids on paper chromatograms with a silver nitrate reagent is described ; silver nitrate-sodium hydroxide was used to detect acids having a *vic.*-glycol or α-keto group. The R_F values for 30 acids in two solvent systems are recorded.

I. INTRODUCTION

Much of the early work on the occurrence of organic acids in fruit was unreliable because the acids were not usually isolated and the analytical methods lacked specificity. In the relatively few cases where acids were isolated, the methods used were of limited application. Nelson (1924) successfully applied the ester distillation technique to the study of fruit acids, but this method is unsatisfactory for esters of low volatility or for the investigation of minor constituents. More recently organic acids have been separated by means of elution chromatography using columns of cellulose (Long, Quayle, and Stedman 1951), silica (e.g. Isherwood 1946), or ion-exchange resins (e.g. Owens, Goodban, and Stark 1953). Owing to the low capacity of any columns used for elution chromatography, attempts to isolate the minor acids of fruits would require unduly large columns for the initial separations. The possibility of using displacement chromatography, where the columns have a large capacity (Tiselius 1952), was therefore explored.

Davies, Hughes, and Partridge (1950) showed that amino acids could be separated by the displacement method on a strongly basic resin if the pK values for the process $-COOH \rightleftharpoons -COO^- + H^+$ were sufficiently far apart. Hulme (1951), using a single column, obtained some separation of quinic acid from malic acid on a weakly basic exchanger, and had better results with the strongly basic resin " Dowex 2 ". Using multiple columns (as in Partridge and Brimley's (1952) separation of amino acids) and strongly basic resins of low cross-linkage,

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† Division of Food Preservation and Transport, C.S.I.R.O., Homebush, N.S.W.

an excellent separation of a large number of organic acids has now been achieved with both synthetic and naturally-occurring mixtures. Some of the results have been described in a preliminary report (Anet and Reynolds 1953).

TABLE 1

ORDER OF EMERGENCE OF ACIDS FROM ANION-EXCHANGE COLUMNS

Acids in Order of Emergence	pK_1 Values at 25 °C*		
	Monobasic Acids	Dibasic Acids	Tribasic Acids
Acetic	4·73		
Lactic	3·86		
Glycollic	3·82		
Quinic	3·66†		
Glyceric	3·55		
Galacturonic	3·42‡		
Glutaric		4·33	
β-Hydroxyglutaric		—	
Succinic		4·17	
β-Hydroxy-β-methylglutaric		—	
Glucuronic	3·33		
α-Hydroxyglutaric		—	
Citramalic		—	
Malic		3·40	
Mucic		—	
Saccharic		—	
Tricarballylic			3·66
Tartaric		2·99	
*iso*Citric			—
Citric			3·09
Malonic		2·76	
Phosphoric		2·13§	
*iso*Citric lactone		—	
α-Ketoglutaric		—	
Oxalic		1·27	
Maleic		1·93	
Hydrochloric	—		

* pK_1 values from Heilbron and Bunbury (1935) except those for galacturonic acid (Speiser, Hills, and Eddy 1945), glucuronic acid (Pauli, Kölbl, and Linsker 1937), and phosphoric acid (Latimer and Hildebrand 1940).

† Determined at 9 °C.

‡ Determined at 27 °C.

§ Phosphoric is here classed as a dibasic acid because of its extremely low pK_3 value (pK_3 12 ; Latimer and Hildebrand 1940).

II. Separation of Acids on Anion-Exchange Resins

The anion-exchange resins used were " Dowex 1–X4 ", " Dowex 2–X4 ", and " Amberlite IRA–400 ", all monofunctional strong bases of the quaternary ammonium type with a cross-linked polystyrene matrix. The resins were packed into columns of decreasing diameter (Partridge and Brimley 1952) and sets of three or more columns were used for each chromatogram. A solution of acids

was run onto the top (largest) column and the mixture was resolved by displacement with 0·1N hydrochloric acid (Anet and Reynolds 1953; cf. Davies and Hughes 1954). The emergent solution was collected in fractions which were examined by means of paper chromatography.

For acids of a given basicity the order of emergence from the columns was in accordance with the pK_1 value (Table 1). Dibasic acids displaced appreciably stronger monobasic acids, and tribasic acids displaced slightly stronger dibasic acids. The behaviour of unsaturated acids was anomalous probably due to

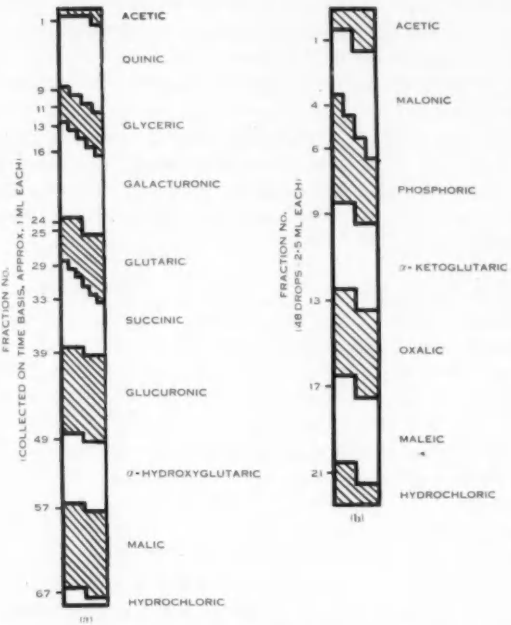

Fig. 1.—Separation of acids on anion-exchange columns showing the approximate proportions of the acids in each fraction.
(*a*) Example 1, Section IV, 0·5 mmole of glyceric acid, 1 mmole of other acids on "Dowex 1–X4".
(*b*) Example 2, Section IV, 1 mmole of each acid on "Dowex 2–X4".

adsorption on the aromatic skeleton of the resins. Maleic acid displaced oxalic acid, itaconic acid (pK_1 3·85) trailed through malic, citric, and the intervening acids, whilst aconitic acid (pK_1 2·80) only emerged as an elution band well behind the hydrochloric acid front. Two examples of the separation of arbitrary mixtures of known acids (examples 1 and 2, Section IV, p. 271) are shown in Figure 1.

The order of emergence of acids shown in Table 1 was derived from a series of such experiments.

The capacity (over 3 m-equiv/g) of these anion-exchange resins is large enough to make displacement chromatography valuable for the purification of acids on a preparative scale, particularly with hydroxy-acids which are often difficult to crystallize or to purify by other means. In example 3 (Section IV), it is shown that glycollic acid was easily separated from its dimer as well as from neutral glycollide and other impurities. The method has also been found useful for the purification of lactic, glyceric, and α-hydroxyglutaric acids.

Both the hydroxide and the acetate forms of the resins were used for the separation of acids. The hydroxide form permits the separation of the widest range of acids but it has several disadvantages; carbon dioxide must be rigidly excluded to avoid the evolution of gas within the columns (cf. Partridge and Brimley 1952, p. 631), resins of low cross-linkage swell excessively, and acids extracted from fruit must be free from reducing sugars which would be degraded to acids on the resin (Phillips and Pollard 1953). None of these difficulties is encountered with the acetate form, the disadvantage here being that monobasic acids weaker than acetic acid will be lost. However, the very weak monobasic carboxylic acids are nearly all volatile or insoluble in water and can be isolated by other methods.

III. The Isolation of Quinic and Other Acids from the Apricot Fruit

From 1901–1922 investigators (see Winton and Winton 1935) of the organic acids of apricot fruits, variously reported the presence of malic, citric, and tartaric acids, or the absence of one or two of them. Nelson (1924) isolated the esters of L-malic and citric acids from dried apricots and showed that they occurred in the ratio 25 : 10; he was unable to detect any tartaric acid. Using displacement chromatography on anion-exchange resins the absence of tartaric acid has now been confirmed and other acids besides malic and citric acids shown to be present.

An aqueous solution was prepared from an alcoholic extract of apricot fruit and was passed through a column of a sulphonated polystyrene cation-exchanger and then through the weak-base anion-exchanger " Amberlite IR–4B ".* The acids recovered from the " IR–4B " column were separated by displacement chromatography on a set of five columns of " Amberlite IRA–400 " and the organic acids were isolated in a pure state from their appropriate fractions as shown in Table 2.

All five columns of " Amberlite IRA–400 " were at first used in the hydroxide form but, even with carbon dioxide-free solutions, the smaller columns were disturbed by the evolution of carbon dioxide. In the separation shown in Table 2 the three smallest columns were in the acetate form and this difficulty was not encountered. It was subsequently realized that the solution of acids run onto the " Amberlite IRA–400 " columns might have contained traces of

* Instead of passing the solution through the " IR-4B " resin it has since (cf. Anet and Reynolds 1954) been found better to run the effluent from the cation-exchanger onto a column of the strong-base anion-exchanger in the acetate form. This column is coupled above two or more smaller columns of the same resin in the acetate form and the acids are separated directly by displacement as described.

reducing sugars eluted from the " IR-4B " column (cf. Reynolds 1955). Consequently the investigation of unknown acids present in trace amounts was deferred until the acids could be run on a set of columns in the acetate form (Anet and Reynolds 1954).

L-Malic, citric, *l*-quinic, and succinic acids were isolated in crystalline form and identified. *l*-Quinic and succinic acids have not been previously detected in the apricot fruit and L-malic and citric acids have not previously been isolated in the free state. The proportion (expressed as moles per cent.) of the various acids in the acid fraction was : malic 76, citric 16, quinic 3, phosphoric 2, succinic plus others 3. Another sample of apricots picked from the same orchard in 1950 gave almost identical results ; the acid fraction contained less malic acid (70 moles per cent.) with a corresponding increase in the amount of citric acid.

TABLE 2

DISPLACEMENT CHROMATOGRAM OF THE ACIDS FROM APRICOTS (1952 SEASON)

Fraction No.	Acids in Fraction*
1	Traces of at least three acids, including quinic, which reduced silver oxide
2–7	Quinic acid
8	Quinic, traces of galacturonic acid and of an unknown acid
9–10	The unknown acid and a trace of galacturonic acid
11–12	Succinic acid and traces of other acids
13–175	Malic acid
176	Malic and citric and traces of other acids
177–209	Citric acid
210	Citric acid and traces of other acids
211–216	Phosphoric acid and a trace of another acid
217	Hydrochloric and phosphoric acid, and traces of other acids

* Revealed by paper chromatography.

IV. EXPERIMENTAL

The melting points are uncorrected. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(*a*) *Ion-Exchange Chromatography.*—Sets of glass columns (Nos. 1–7) were made up, the internal diameters being 0·6, 0·9, 1·2, 1·7, 2·5, 3·8, and 5·1 cm respectively. Each column had a glass stop cock at the bottom and a side arm near the top closed with rubber tubing and a screw clip. Glass-wool was rammed tightly into the bottom of the column ; in the larger tubes it was covered with a disk of glass-cloth. The resins were poured into the columns as a slurry in water taking care that no air bubbles were trapped. A polyethylene float was placed on top of the resin bed to break up the drops coming from the column above. Columns were coupled with rubber bungs and by manipulation of the stop cock and screw clip, the level of the liquid was lowered until the float just cleared the resin bed. It was usually necessary to re-adjust the liquid levels at intervals during each run, particularly when separating strong acids which cause the resins to shrink.

The three resins used were " Amberlite IRA–400 " (20–50 mesh), " Dowex 1–X4 " (50–100 mesh), and " Dowex 2–X4 " (100–200 mesh). The " Amberlite IRA–400 " was ground wet in a ball mill before sieving ; the other resins were sieved as received. The particle size (mesh/in) and the dry weight (approx.) of resin (hydrochloride form) in each column were : No. 1, <200 mesh, 0·3 g ; No. 2, 100–200 mesh, 1 g ; No. 3, 100–200 mesh, 3 g ; No. 4, 80–100 mesh, 10 g ; No. 5, 80–100 mesh, 30 g ; No. 6, 60–80 mesh, 100 g ; No. 7, 60–80 mesh, 300 g.

Before use, new resins were converted twice to the hydroxide and chloride forms to remove impurities. When used in the hydroxide form for chromatography, the resins were regenerated with carbonate-free sodium hydroxide and washed with carbon dioxide-free water. When used in the acetate form the resins were regenerated with 2N sodium hydroxide, treated with 1N sodium acetate, and washed with 0·1N acetic acid to remove the sodium ions ; the omission of a water wash prevented the excessive swelling of resins which had a low cross-linkage.

A solution containing the acids to be separated (total molarity *c.* 0·1M) was run onto the top column of a set so that the acids occupied no more than three-quarters of the top (largest) column. When the solution had been added, it was run down to the level of the resin in the top column. The acids were then displaced with 0·1N hydrochloric acid added from a separating funnel through a polyethylene tube, the flow rate being regulated by adjusting the height of the funnel. With column No. 1 at the bottom of the set the flow rate used was 7·5 ml/hr, with No. 2 at the bottom 15 ml/hr, with No. 3, 30 ml/hr, etc. These flow rates gave good separations which could be made a little sharper by halving the flow rate. The number of columns used depended on the desired resolution ; even with acids which are easily separated an overlap amounting to at least a tenth of the capacity of the smallest column is to be expected. A column of 0·3 g of resin is close to the minimum practical size, and with a smaller bottom column, the flow rate must be correspondingly slow if the full advantages of the small cross-sectional area are to be obtained. The acid front could usually be seen on the cream coloured resin. The stronger acids usually appeared as lighter bands probably because of a pH effect ; however, citric acid gave a lighter colour to the resin than hydrochloric acid. The acids emerged in approx. 0·1M solutions which were collected on an automatic fraction collector actuated by a drop counter or a clock.

(i) *Example 1.* Quinic, galacturonic, glutaric, succinic, α-hydroxyglutaric, and malic acids (1 mmole of each), the sodium salt of glucuronic acid (1 mmole), and glyceric acid (0·5 mmole) were made up to 75 ml with water. The solution was run at a flow rate of 7·5 ml/hr on to columns Nos. 4–1 in series packed with " Dowex 1–X4 " in the acetate form. The mixture was then displaced by 0·1N hydrochloric acid at the same flow rate. The effluent solution was collected in approx. 1 ml fractions (12 fractions/hr) which were examined by paper chromatography (see Fig. 1 (*a*)).

(ii) *Example 2.* One mmole each of malonic, phosphoric, α-ketoglutaric, oxalic, and maleic acids was made up to 50 ml. The solution was run at a flow rate of 7·5 ml/hr onto the columns Nos. 3–1 in series packed with " Dowex 2–X4 " in the acetate form. The mixture was then displaced by 0·1N hydrochloric acid at the same flow rate. Fractions of 2·5 ml each were collected and examined by paper chromatography (see Fig. 1 (*b*)).

(iii) *Example 3.* Purification of " B.D.H. commercial glycollic acid 65–67%." The acid (35 ml diluted to 2000 ml with water) was run, at a flow rate of 360 ml/hr, onto columns Nos. 6 and 5 in series packed with " Dowex 1–X4 " in the acetate form. The mixture was then displaced by 0·1N hydrochloric acid at a flow rate of 120 ml/hr. Two well-separated dark brown bands could be seen on the columns in between the glycollic and hydrochloric acid bands. When the bottom band approached the bottom of column No. 5, column Nos. 4–2 packed with the same resin, were attached and the flow rate was progressively reduced to 15 ml/hr as the coloured band reached the smallest column. The displacement was continued until hydrochloric acid appeared. The effluent was collected in fractions of decreasing size. Using paper chromatography it was shown that solutions of the components of this mixture emerged in the following order : (1) pure glycollic acid (3010 ml), (2) a dark brown solution containing a mixture of glycollic acid, an unknown yellow coloured acid, and glycolloglycollic acid (40 ml), (3) a mixture of the yellow acid and glycolloglycollic acid (40 ml), (4) pure glycolloglycollic acid (170 ml), (5) a yellow solution containing a mixture of acids, including monochloroacetic (80 ml). The glycollic acid fractions were concentrated and yielded the acid, m.p. 78 °C (Found : C, 31·9 ; H, 5·4% ; equiv. wt. 75. Calc. for $C_2H_4O_3$: C, 31·6 ; H, 5·3% ; equiv. wt. 76). On concentration the glycolloglycollic acid fraction yielded the acid which was recrystallized from methyl ethyl ketone, m.p. 98 °C (Found : C, 36·0 ; H, 4·7% ; equiv. wt. 135. Calc. for $C_4H_6O_5$: C, 35·8 ; H, 4·5% ; equiv. wt. 134).

The order of emergence of 27 acids from sets of anion-exchange columns is shown in Table 1.

(*b*) *Paper Chromatography.*—Chromatograms were run by the descending method on No. 1 Whatman paper. The solvents used were methyl ethyl ketone-cineole-aqueous formic acid (53% w/v) (50 : 50 : 36 v/v) (Anet and Reynolds 1953) (solvent *A*), and ethanol (95%)-ammonia-water (80 : 5 : 15 v/v) (Long, Quayle, and Stedman 1951) (solvent *B*). R_F values for 30 acids in these solvents are shown in Table 3.

TABLE 3

BEHAVIOUR OF ACIDS ON PAPER CHROMATOGRAMS

Acid	Solvent *A** $R_F \times 10^2$	Solvent *B*† $R_{Lactic} \times 10^2$
Mucic‡	0	35
Galacturonic‡	3	Decomp.
Glucuronic‡	3	Decomp.
Quinic‡	7	77
Hydrochloric	6 and 11	100
Tartaric‡	12	32
Phosphoric	16	6
Glyceric‡	17	79
Citric§	19	10
*iso*Citric§	20	10
Malic	26	40
β-Hydroxyglutaric	31	50
Glycollic	34	87
α-Hydroxyglutaric	34	50
Citramalic	38	50
*iso*Citric lactone§	40	Hydrolysed
Tricarballylic	44	17
α-Ketoglutaric‡	47	60 (decomp.)
Oxalic	48 (trailing)	Streak
Malonic	49	30
β-Hydroxy-β-methylglutaric	52	65
Maleic	54	45
Lactic	54	100
Succinic	56	50
Glutaric	64	60
Aconitic	67	18
Itaconic	68	55
Fumaric	76	60
Chloroacetic	83	105
Trichloroacetic	88	140

* Solvent *A* was methyl ethyl ketone-cineole-aqueous formic acid (53% w/v) (50 : 50 : 36 v/v) (Anet and Reynolds 1953).

† Solvent *B* was ethanol (95%)-ammonia-water (80 : 5 : 15 v/v) (Long, Quayle, and Stedman 1951). These R_{Lactic} values were obtained on washed papers.

‡ These acids gave a black spot on paper chromatograms with the silver nitrate-sodium hydroxide reagent (Section IV (*b*)); galacturonic and glucuronic acids darkened immediately, the others after 1–2 min. All other acids in this table gave a white spot.

§ Citric and *iso*citric acids can be distinguished by converting *iso*citric acid to the lactone by heating at 100 °C under reduced pressure. The lactone was not formed when a solution of the acid was boiled.

Papers run in solvent *A* were allowed to dry for 3 hr at room temperature. The acids were then revealed by rapidly pulling the paper through a solution of silver nitrate (3 ml of 50% aq. soln. w/v) in acetone (200 ml), followed by (i) heating the paper for a few minutes at 100 °C, and/or (ii) spraying it with sodium hydroxide (4 ml sat. aq. soln. in 100 ml of 95% ethanol). The chromatogram was then fixed in sodium thiosulphate (5%), washed, and dried. After treatment (i) all acids gave a white spot on a grey background ; after treatment (ii) acids having a *vic.*-glycol or an α-keto group gave an intense black spot on a grey, or white (if not heated), background (cf. Anet and Reynolds 1954) (see Table 3). Papers run in solvent *B* were dried at 90 °C for 5 min and then sprayed with a universal indicator solution adjusted to pH 8 (Long, Quayle, and Stedman 1951), or treated with the reagent described above.

(c) *Acids in Apricot Fruits.*—The apricot fruits (variety Trevatt) were picked from an orchard at Wedderburn, N.S.W., in December 1952. Eating-ripe fruits (100 g ; without pits) were cut into slices, dropped into ethanol (95% ; 325 ml) in a blendor running at full speed, and a further 100 ml of ethanol was added. The blending was continued for a further 2½ min. This 80% ethanolic extract was filtered and then evaporated under reduced pressure at 30 °C to a syrup, which was taken up in water and filtered through " Dicalite 4200 ". The combined aqueous extract from 1200 g fruit was made up to 2 l. and was 0·100N when titrated with sodium hydroxide using phenolphthalein as an indicator.

The aqueous extract was passed at a flow rate of about 10 ml/min through 2 ion-exchange columns in series ; first a cation-exchanger (" Zeo-Karb 225 " 4½% cross-linked ; 90 g) in the acid form, and then a weak base anion-exchanger (" Amberlite IR–4B " ; 130 g) in the basic form. The columns were then washed with water (500 ml) and disconnected. The " IR–4B " column was washed with a further 2·5 l. of water and the acids were eluted from the resin with 2N ammonia (1300 ml). Excess ammonia was evaporated off under reduced pressure and the remainder was removed by passing the solution through a column of " Zeo-Karb 225 " in the acid form. The solution which was then freed from carbon dioxide by partial evaporation under reduced pressure, contained only the fruit acids which were soluble in both 80% ethanol and water.

This solution of acids from the apricot was passed at a flow rate of 15 ml/hr through a series of five columns (Nos. 6–2) of " Amberlite IRA–400 ". Columns 6 and 5 were both in the hydroxide form (free from carbon dioxide) and the last three (Nos. 4–2) in the acetate form. When the acids had been added they were displaced by 0·1N hydrochloric acid at the same flow rate. The effluent was collected on an automatic fraction collector, fractions 1–57 each had a volume of 5 ml and fractions 58 upwards 6 ml each. The acids in each fraction were revealed by paper chromatography and some were isolated (see Table 2).

(i) *Isolation of* l-*Quinic Acid.* Fractions 4, 5, and 6 were combined and evaporated under reduced pressure. The residue crystallized on addition of dry ether. The crystals were washed twice with hot acetone and then dissolved in aqueous acetone ; a trace of amorphous impurity was precipitated by adding ether. The solvent was evaporated under reduced pressure and the residue was crystallized from water as colourless prisms, m.p. 166–168 °C not depressed by an authentic sample, $[\alpha]_D^{20}$ —42±2° (in water) ; Pigman and Goepp (1948) give m.p. 162 °C and $[\alpha]_D^{20}$ —44° for *l*-quinic acid (Found : C, 43·6 ; H, 6·2% ; equiv. wt. 193. Calc. for $C_7H_{12}O_6$: C, 43·7 ; H, 6·2% ; monobasic acid equiv. wt. 192). The acid was chromatographically identical with *l*-quinic acid in solvents *A* and *B*.

(ii) *Isolation of Succinic Acid.* The ethyl acetate-soluble portion of fractions 11 and 12 was dissolved in hot water and on cooling to 0 °C succinic acid crystallized out, m.p. 182–183 °C not depressed by an authentic sample. It was chromatographically identical with succinic acid in solvents *A* and *B* and in a two-dimensional chromatogram in those two solvents.

(iii) *Isolation of* L-*Malic Acid.* Fractions 17 to 173 were combined and evaporated under reduced pressure to a crystalline mass which was dissolved in acetone. Dry ether precipitated a small amount of insoluble matter which was filtered off and the filtrate, after concentration, yielded crystals which were washed with ether and dried, m.p. 102–103 °C not depressed by an authentic sample (Found : C, 36·1 ; H, 4·7% ; equiv. wt. 68. Calc. for $C_4H_6O_5$: C, 35·8 ; H, 4·5% ; dibasic acid equiv. wt. 67). The acid was chromatographically identical with L-malic

acid in solvents *A* and *B*. The molybdenum complex (264 mg acid plus 664 mg ammonium molybdate made up to 25 ml with water) gave $[\alpha]_D^{20}$ +633°. Authentic L-malic, from Messrs. L. Light & Co., purified as above gave $[\alpha]_D^{20}$ +634° under the same conditions. McKenzie and Plenderleith (1923) give $[\alpha]_D^{15.5}$ +568° for similar conditions.

(iv) *Isolation of Citric Acid.* Fractions 180 to 209 were combined and evaporated under reduced pressure to a syrup which crystallized. The crystals were dissolved in acetone, treated with charcoal, crystallized from acetone-ether, recrystallized from water, and dried at 50 °C *in vacuo*, m.p. 153 °C not depressed by an authentic sample, equiv. wt. 65, calc. for tribasic acid 64. The pentabromoacetone derivative (Wilson 1950) had m.p. 72 °C not depressed by an authentic sample. The acid was chromatographically identical with citric acid in solvents *A* and *B*.

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WATER-SOLUBLE CONSTITUENTS OF FRUIT

III. AN EXAMINATION OF THE SUGARS AND POLYOLS OF APRICOTS, PEACHES, PEARS, AND APPLES BY PAPER CHROMATOGRAPHY

By A. S. F. Ash* and T. M. Reynolds*

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Summary

The sugars and polyols in 80 per cent. ethanolic extracts of apricots, peaches, pears, and apples were examined by paper chromatography using several solvents. Xylose, fructose, glucose, sucrose, sorbitol, a cyclitol (probably *meso*inositol), and one or more ketose oligosaccharides were detected in all the fruits. Galactose was detected in pears and may also be present, in trace amounts, in peaches and apples. Apricots, peaches, and pears picked in several seasons were examined.

I. Introduction

The percentages of glucose, fructose, and sucrose (assumed to be the predominant sugars) in apricots, peaches, pears, apples, and other fruits have been determined by Widdowson and McCance (1935). These sugars, and also xylose, were later detected in apples by paper chromatography (Aso and Matsuda 1951) and the presence of xylose confirmed by the preparation of the phenylosazone.

Sorbitol has been isolated from pear fruit as the pyridine complex (Strain 1937) and as the hexa-acetate or benzal derivative from apples (Tutin 1925), peaches, pears, apricots, and many other fruits (Vincent and Delachanal 1889; Reif 1934). *meso*Inositol has been isolated from citrus juices by Nelson and Keenan (1933) but its occurrence in other fruit has not been reported. A previous communication (Ash and Reynolds 1954*b*) appears to be the first report of ketose oligosaccharides in fruit. The occurrence of galactose in fruit has not been noted previously.

II. Methods

(*a*) *Fruit Extracts.*—The extracts were prepared as described in Part I of this series (Ash and Reynolds 1954*a*) and were not de-ionized. In many cases the same extracts were used in both investigations.

(*b*) *Paper Chromatography.*—(i) *General.* The technique and the three reagents (silver nitrate-sodium hydroxide, aniline phosphate, and naphthoresorcinol-trichloroacetic acid) used previously (see Ash and Reynolds 1954*a*) were unmodified. Bromocresol purple-borax (Bradfield and Flood 1950), which reacted preferentially with hexitols, was used as an additional reagent. An extract of each type of fruit was also examined for heptoses using an orcinol spray (Klevstrand and Nordal 1950). The solvents used were ethyl acetate-pyridine-water (8 : 2 : 1 v/v) (White and Secor 1953), *n*-butanol-acetic acid-water (4 : 1 : 1 v/v), and phenol-water (4 : 1 w/v); the usual times for the development of chromatograms were 16–24, 64, and 48 hr respectively. The

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sugars and polyols were recognized by comparing their reactions and the distances run with those of authentic compounds on the same chromatograms.

Some extracts were also examined by two-dimensional paper chromatography using *n*-butanol-acetic acid-water (4 : 1 : 1 v/v) and phenol-water (4 : 1 w/v) as solvents.

(ii) *Semi-quantitative Estimations.* The sugars and polyols in selected extracts were estimated by visual comparison of spots on paper chromatograms, using as standards known amounts of authentic sugars and polyols applied as spots (2 μl) containing 1–8 μg of solid. The volume of extract, or diluted extract, used was such that the concentration of the sugar or polyol being estimated fell within this range. Melezitose was used as a standard for the ketose oligosaccharides. An " Agla " microsyringe was used to apply the spots to the starting line.

The silver nitrate reagent was used for polyols and for all sugars except sucrose and the ketose oligosaccharides which were sprayed with naphthoresorcinol-trichloroacetic acid.

III. Results

Ripe apricots, peaches, pears, and apples (5, 6, 9, and 1 samples respectively) were used in these experiments. The fruit was mature when received and was ripened at 20 °C where necessary. The varieties, and the seasons in which the samples were picked, are shown in Table 1. The 80% ethanolic extracts prepared from these samples were used for paper chromatography without further treatment. Approximately 30 μl of extract (≡6·4 mg of fresh fruit) were used for one-dimensional chromatograms, and 60 μl for two-dimensional chromatograms. These quantities gave compact sugar spots which were neither distorted by the acids and bases present nor improved by their removal with ion-exchange resins. The use of heavier loads did not increase the number of minor constituents which could be detected except for an additional oligosaccharide in pears (see below).

Each fruit species gave a characteristic pattern of spots. The two-dimensional chromatograms did not reveal any sugars or polyols not detected in one or other of the three solvents used for one-dimensional chromatograms. The substances detected (Table 1) included a compound presumed to be a cyclitol from its neutral nature, R_F value, reaction with the silver nitrate reagent, and absence of reaction with the other reagents. Heptoses were not detected in any of the fruits. Within each species there were visible variations in the concentrations of minor constituents; spots given by major constituents were too heavy for the detection of variations within a species.

An estimate of the concentration of each constituent was obtained by visual comparison of spots of low concentration (1–8 μg; Section II (*b*) (ii)) using one sample of each species. The results obtained are shown in Table 1. The xylose content was less than 0·2 per cent. throughout but the percentage in pears was 3–10 times that in other fruits.

The small amount of galactose present in pears could be detected with either aniline phosphate or silver nitrate-sodium hydroxide. In apples and peaches only a faint fluorescence was detected in the appropriate position on paper chromatograms sprayed with aniline phosphate. Ethyl acetate-pyridine-water was the most satisfactory solvent for studying the occurrence of both galactose and the hexitol. Although the spots due to galactose and sorbitol were in juxtaposition or slightly overlapping, galactose was well separated from the other sugars and could be differentiated from sorbitol by the use of aniline phosphate which does not react with hexitols. Sorbitol was distinguished from the sugars, with the exception of fructose, by the bromocresol purple-borax reagent. Fructose reacted with the reagent but was well separated from sorbitol in this solvent.

It has now been shown (Ash and Reynolds 1954*b*) that the apricot fruit contains a number of oligosaccharides some of which cannot be detected on paper chromatograms. In the apricot oligosaccharides *A* and of *B* Table 1 correspond with those previously designated K1 and K3. In the other fruits oligosaccharide *A* had the same R_F as K1; oligosaccharide *B* had the same R_F as K3 except in Golden Queen peaches and Packham's Triumph pears where the R_F was slightly lower. On paper chromatograms K3 has an R_F very close to that of melezitose and K1 lies between melezitose and sucrose. Although the oligosaccharides all appear as minor constituents in Table 1 there was a marked and consistent variation between species in the apparent

TABLE I

THE OCCURRENCE OF SUGARS AND POLYOLS IN APRICOTS, PEACHES, PEARS, AND APPLES

Fruit	Fruit and Variety*	Year†	Sugars and Polyols Detected‡								
			Glucose	Fructose	Sucrose	Xylose	Galactose	Oligosaccharide *A*	Oligosaccharide *B*	Sorbitol	Cyclitol
Apricots	Trevatt	1949	+++	++	Predominant	+	—	+	+	++	+
	,, ...	1950									
	,, ...	1951									
	,, ...	1952									
Peaches	Blackburn Elberta	1950	+++	++	Predominant	+	+ (?)	—	+	+	+
	,, ,,	1951									
	,, ,,	1952									
	,, ,,	1954									
	J. H. Hale	1950									
	Golden Queen ..	1950									
Pears	Packham's Triumph	1950	+++	Predominant	++	+	+	+	+	++	+
	,, ,,	1952									
	Josephine	1950									
	Winter Cole ..	1950									
	,, ,, ..	1951									
	,, ,, ..	1952									
Apples ..	Granny Smith ..	1951	+++	Predominant	+++	+	+ (?)	+	+	++	+

* All the apricots (except for one sample collected from Leeton in 1949) and all the Blackburn Elberta peaches came from the same orchard at Wedderburn (N.S.W.). The J. H. Hale peaches came from Bathurst, and the Golden Queen peaches from Leeton. The pears came from Bathurst, Orange, and Batlow.

† Two samples of apricots were collected in 1949 ; two samples of Winter Cole pears were collected in 1950, and three in 1951.

‡ The approximate concentrations of the sugars and polyols are indicated by symbols as follows : —, not detected ; +, minor (<0·2% of the fresh fruit) ; ++, intermediate concentration (max. 1·5%) ; +++, major (max. 3%) ; predominant (>3%).

concentrations. Oligosaccharide *A* was relatively strong in pears and much weaker in apricots and apples; oligosaccharide *B* was relatively strong in apricots and weak in the other fruits.

An additional oligosaccharide was detected when an extract of Winter Cole pears was run in high concentration on No. 3 MM Whatman papers (Ash and Reynolds 1954*a*, p. 439). This oligosaccharide had a lower R_F than K3 and gave a pink colour with aniline phosphate. It was eluted from the chromatograms and hydrolysed with 85 per cent. formic acid; xylose, glucose, and traces of fructose were then detected by paper chromatography.

IV. Discussion

This work supports the widely held view that glucose, fructose, and sucrose are present in apricots, peaches, pears, and apples. A pentose, having the properties of xylose, was detected in all fruits. For apples, the presence of xylose is confirmed by the work of Aso and Matsuda (1951) (cf. Section I). The detection of galactose in peaches and apples was uncertain but in pears there was clearly a sugar with the same R_F values and reactions. The hexitol detected in this investigation was presumably sorbitol as this has been isolated by earlier workers (Section I). However, mannitol, or even dulcitol, could also be present since these have the same R_F values. The cyclitol was probably *meso*inositol but other cyclitols cannot be excluded since their reactions on paper are the same and the R_F values are low in the solvents used. The ketose oligosaccharides detected in the various species of fruit were probably all closely related compounds. It is expected that, as in the apricot (Ash and Reynolds 1954*b*), other ketoses occur in concentrations below the limits of detection on paper.

The concentrations of glucose, fructose, and sucrose (see Table 1) were of the same order as those found for aldose, ketose, and non-reducing sugar in the same fruits by Widdowson and McCance (1935).

The characteristic pattern of spots given by the different crops and varieties of each species of fruit was a notable feature of the work. This suggests that it is unnecessary to examine large numbers of samples of a species in order to obtain a picture of the sugars and polyols present and that it is justifiable to use only a very few samples when making detailed qualitative studies.

V. Acknowledgments

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WATER-SOLUBLE CONSTITUENTS OF FRUIT

IV. THE ORGANIC ACIDS IN PEACHES

By E. F. L. J. Anet* and T. M. Reynolds*

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Summary

The acids in several varieties of peaches were separated by displacement chromatography on strongly basic anion-exchange resins. *l*-Quinic, L-malic, and citric acids were the three main acids, any one of them being the predominant acid depending on the variety, season, and maturity of the fruit. Mucic acid was found in small quantity in all samples; galacturonic acid was only present in fruit picked at commercial maturity and ripened at 20 °C. The effect of maturity on the three major acids was studied for one crop of Blackburn Elberta peaches; the immature fruit contained only traces of citric acid.

I. Introduction

Using the ester-distillation method, Nelson (1924) found L-malic and citric acids in peaches in approximately equal proportions. However, Peynaud (1951) showed that these acids accounted for only 40–80 per cent. of the total acidity of the fruit. Hulme and Swain (1951), using paper chromatography, found that the peach fruit contained an acid which had the same R_F value as an unknown acid in apples. Hulme (1951) isolated the unknown acid from immature apples and showed that it was *l*-quinic acid. Displacement chromatography on anion-exchange resins has shown that *l*-quinic acid occurs in quantity in ripe peaches and some of the results have been described in a preliminary report (Anet and Reynolds 1953). The present paper amplifies the earlier report and describes additional work on a later crop of peaches as well as a modification of the technique for ion-exchange chromatography recently described in full (Anet and Reynolds 1955).

II. Methods

(*a*) *Fruit Extracts.*—The preparation of 80 per cent. ethanolic extracts of fruit and the derivation of aqueous extracts therefrom was carried out as described previously (Anet and Reynolds 1955, Section IV (*c*)).

(*b*) *Ion-Exchange Chromatograms.*—In the early experiments (using fruit picked in 1950–52) the acids were collected after removal of the cations, on a column of the weak-base anion-exchanger "Amberlite IR–4B" and subsequently fractionated on a set of columns of "Amberlite IRA–400" in the hydroxide form (Anet and Reynolds 1953, 1955, Section IV (*c*)).

In the later experiments the aqueous extract was run through a cation-exchanger (sulphonated polystyrene) and thence straight onto a column of a strong-base anion-exchanger ("Amberlite IRA–400") which was in the acetate form (Anet and Reynolds 1954) and saturated with 0·1N

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acetic acid. This column was placed on top of two or more columns of the same resin in the acetate form and, without any preliminary washing, the acids were displaced with 0·1N hydrochloric acid.

A preliminary identification of the acids in the various fractions was deduced from paper chromatograms (using the solvents and reagents described by Anet and Reynolds 1955) and from the order of emergence of the acids from the columns. Using 0·1N hydrochloric acid for displacement, the acids emerged in 0·1M solution (checked by titration) and the molar proportions were calculated from the volumes.

To isolate the acids, the fractions containing a single acid were combined and evaporated to dryness under reduced pressure. The acids then crystallized and were recrystallized to constant m.p.

III. Results

The acids present in six different crops of peaches are shown in Table 1. For the 1951 crop of Blackburn Elberta peaches, the acids from 2 kg of fruit were separated on a set of five columns (Nos. 6–2) (Anet and Reynolds 1955, Section IV (*a*)); *l*-quinic, L-malic, and citric acids were crystallized and identified and the fractions containing a uronic acid were oxidized with

Table 1

ACIDS IN SIX CROPS OF PEACHES*

Expressed as moles per cent. of total acids

Experimental Details	Blackburn Elberta from Wedderburn, N.S.W.				J. H. Hale from Bathurst, N.S.W.	Golden Queen from Leeton, N.S.W.
	1950	1951	1952	1954	1950	1950
Quinic acid	28	40	38	24	18	16
Malic acid	40	30	20	28	47	64
Citric acid	25	22	36	34	28	12
Phosphoric acid	5	4	½	5	5	5
Galacturonic acid	?	2	3	6	?	?
Other acids	2	2	2½	3	2	3
Acidity A†	6·2	9·6	8·4	9·0	12·1	5·7
Acidity B†	9·6	14·0	12·8	12·7	16·1	10·2
Total solids (%)	13·0	17·3	17·2	10·5	12·7	14·0

* The Blackburn Elbertas of 1950 were tree-ripe; the other crops were picked at or after commercial maturity and were ripened for varying periods at 20 °C. The 1954 crop of Blackburn Elbertas was taken from one large tree.

† The titration figures for the fruit extract before (acidity A) and after (acidity B) passing through the cation-exchanger—expressed as the number of ml of N alkali required to neutralize the extract from 100 g of fruit.

nitric acid giving mucic acid (Anet and Reynolds 1953). The treatment of the 1954 crop of Blackburn Elbertas is described below. For the other 1950–52 crops the acids from 200 g of fruit were separated on three columns (Nos. 4–2) and identified by paper chromatography and their order of emergence from the columns.

The acids from 1700 g of fruit from the 1954 crop of Blackburn Elbertas were separated on five columns (Nos. 6–2) of " Amberlite IRA–400 " in the acetate form. The composition of the fractions collected is shown in Table 2. The details of the final identification of five acids

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follow. (The melting points are uncorrected. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory):

(i) l-*Quinic Acid*. The acid was recrystallized from water, m.p. 168–169 °C not depressed by an authentic sample; $[\alpha]_D^{20}$ —44° (*c*, 0·04 in water) (cf. Anet and Reynolds 1953). Pigman and Goepp (1948) give m.p. 162 °C and $[\alpha]_D^{20}$ —44° but Grewe, Lorenzen, and Vining (1954) found m.p. 168 °C and $[\alpha]_D^{23}$ —43° for synthetic *l*-quinic acid (Found: C, 43·8; H, 6·2%; equiv. wt. 191. Calc. for $C_7H_{12}O_6$: C, 43·7; H, 6·3%; monobasic acid equiv. wt. 192).

(ii) D-*Galacturonic Acid*. Fractions 38–45 inclusive (Table 2) contained substantially galacturonic acid and, after evaporation under reduced pressure, this acid crystallized. The acid crystallized from 95% ethanol in the β-form as needles, m.p. 158–159 °C (decomp. 165–166 °C); or from water (evaporated under reduced pressure) as the monohydrate of the α-form, sintered

TABLE 2

ION-EXCHANGE CHROMATOGRAM OF ACIDS FROM 1954 CROP OF BLACKBURN ELBERTA PEACHES

Fraction No. (each 6·5 ml)	Contents of Fractions
1	Acetic acid (from column) and traces of other acids
2–36	Quinic acid
37	Quinic and galacturonic acid
38–45	Galacturonic acid and a very small amount of another acid (all fractions)
46–49	Mixture, including succinic and numerous other acids
50–90	Malic acid
91	Malic acid; very small precipitate of mucic acid
92	Malic and citric acids; precipitate of mucic acid and traces of other acids
93	Citric acid; precipitate of mucic acid
94–143	Citric acid
144	Citric acid and some phosphoric acid
145–151	Phosphoric acid
152	Phosphoric acid; a small white precipitate and other minor acids
153	Hydrochloric acid

110 °C, m.p. 156–158 °C (decomp.) (Found for anhydrous sample: C, 36·7; H, 5·4; O, 57·5%. Calc. for $C_6H_{10}O_7$: C, 37·0; H, 5·3; O, 57·7%), $[\alpha]_D^{20}$ (equilibrium) +55° (in water). These constants for α- and β-D-galacturonic are consistent with those given in the literature (Kertesz 1951). Oxidation of the acid with nitric acid yielded mucic acid, m.p. 216 °C (decomp.).

(iii) L-*Malic Acid*. The acid crystallized as needles from acetone-ether, m.p. 102–103 °C not depressed by an authentic sample; $[\alpha]_D^{20}$ +630° for the molybdenum complex (Anet and Reynolds 1955) (Found: C, 36·2; H, 4·6%; equiv. wt. 68. Calc. for $C_4H_6O_5$: C, 35·8; H, 4·5%; dibasic acid equiv. wt. 67).

(iv) *Citric Acid*. The acid crystallized as the monohydrate from water, m.p. 153 °C (anhydrous) not depressed by an authentic sample; optically inactive (Found for anhydrous sample: C, 37·5; H, 4·3%; equiv. wt. 63. Calc. for $C_6H_8O_7$: C, 37·7; H, 4·2%; tribasic acid equiv. wt. 64).

(v) *Mucic Acid*. The acid (85 mg) crystallized out on standing for several days at +1 °C from fractions 91, 92, and 93 (Table 2). The crystals were dissolved in sodium hydroxide, filtered,

acidified with HCl and allowed to stand at +1 °C. The acid crystallized as needles, m.p. 215 °C (decomp.) not depressed by an authentic sample. The sodium salt was optically inactive (Found : C, 34·2 ; H, 4·8 ; O, 61·0%. Calc. for $C_6H_{10}O_8$: C, 34·3 ; H, 4·8 ; O, 60·9%). The diphenylhydrazide had m.p. 242 °C not depressed by an authentic sample.

Some information on the effect of maturity on the major acids of peaches was obtained from the Blackburn Elberta crop of 1954. When the first sample was picked tags were attached at 4 positions on each of 7 main branches of a tree. At each of the 4 pickings one fruit of about average size was taken from each of the 28 positions. This method of sampling was adopted because Martin (1953) found that the branches of apple trees behaved as organic units. Ethanolic extracts were prepared immediately from each sample without ripening. The acids from about 200 g of fruit were separated on three columns (Nos. 4–2) of " Amberlite IRA–400 " in the acetate form. The acids were recognized by paper chromatography and their order of emergence from the column. The results obtained are shown in Table 3.

TABLE 3

EFFECT OF MATURITY ON THE MAJOR ACIDS IN BLACKBURN ELBERTA PEACHES*

Results		Picking Dates	3.xii.53	21.xii.53	5.i.54	19.i.54
Results—per fruit basis	Weight of whole fruit (g)	..	38	42	67	136
	Total solids of flesh (g)	..	4·2	6·7	8·3	14·4
	Quinic acid (mg)	.. ..	270	310	330	360
	Malic acid (mg)	.. ..	170	230	230	360
	Citric acid (mg)	.. ..	15	70	170	530
Results as per cent. of flesh	Total solids (%)	.. ..	13·4	15·9	12·4	10·6
	Quinic acid (%)	.. ..	0·9	0·9	0·6	0·3
	Malic acid (%)	.. ..	0·5	0·7	0·4	0·3
	Citric acid (%)	.. ..	0·05	0·2	0·3	0·4

* The first three samples were green and hard. Dry weather during December, followed by heavy rain at the beginning of January, delayed the development of the fruit. Fruit picked on January 19 was mature and medium-ripe to ripe.

IV. DISCUSSION

In the course of this work the technique for carrying out the displacement chromatography of the acids was changed (Section II). The reasons for (and the disadvantages of) using the acetate form of the strong-base anion-exchanger in place of the hydroxide form have already been discussed (Anet and Reynolds 1955). Using the acetate form of the resin the natural mixture of acids and neutral substances (i.e. the effluent from the cation-exchanger) can be run straight on to the largest of an appropriate set of displacement columns. Previously the cation-free extract was run on to a column of the weak-base anion-exchanger " Amberlite IR–4B " and the acids were recovered by stripping the column with ammonia. Certain acids, such as galacturonic acid, are liable to be degraded in the presence of ammonia.

l-Quinic, L-malic, and citric acids were the main organic acids found in the three varieties of peaches studied (Table 1). The proportions of these acids varied markedly in the same variety with the season (Table 1) and the maturity

(Table 3). Most of the quinic acid and half of the malic acid were present at the first picking, whereas almost all of the citric acid was formed during the later development. Peynaud (1950), who studied 75 varieties of peaches, found that 17–45 per cent. of the acidity could not be accounted for. The present work suggests that all varieties of peaches may contain a considerable amount of quinic acid.

Mucic acid was present in peaches in trace amounts and has also been found in pears, apricots, passion-fruit, and blackberries (Anet and Reynolds 1954). D-Galacturonic acid was found in peaches which had been ripened at 20 °C for 2 to 8 days ; it was not detected in tree-ripened or green peaches thus confirming the results of Ash and Reynolds (1954) who used paper chromatography only.

V. Acknowledgments

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SHORT COMMUNICATIONS

REACTION KINETICS AT 30000 ATMOSPHERES*

By H. G. David,† S. D. Hamann,† and S. J. Lake†

In this note we describe some measurements of the rate of solvolysis of ethyl chloride in pure methanol at several pressures up to 30000 atm. This pressure is almost twice as great as any hitherto applied in kinetic measurements. We have made the experiments to see whether any new chemical effects appear in the range 15000–30000 atm.

We selected methanol and ethyl chloride as the reactants for the following reasons: (i) it was essential that the reaction mixture should not solidify under compression; methanol is the only highly polar hydroxylic solvent which is still liquid at 30,000 atm, (ii) ethyl chloride is sufficiently unreactive to give a manageably slow rate of reaction over the whole pressure range. The reaction proceeds by the first-order S_N2 mechanism (Ingold 1953)

$$\begin{array}{c} H \quad Cl \\ | \quad | \\ CH_3-O \quad CH_2-CH_3 \end{array} \rightarrow \left[\begin{array}{c} \overset{\delta+}{H} \quad \overset{\delta-}{Cl} \\ \vdots \quad \vdots \\ CH_3-O \ldots CH_2-CH_3 \end{array} \right] \rightarrow H^+ + Cl^- + CH_3-O-CH_2-CH_3, \qquad \ldots\ldots\ldots\ldots (1)$$

with, perhaps, a small amount of side-reaction producing ethylene. The transition state, shown in brackets in (1), is more polar than the initial state, and, from our earlier considerations of the effects of pressure on the solvation free energies of electrically charged groups (Buchanan and Hamann 1953) we expected the reaction to be greatly accelerated by pressure. We found experimentally that it was accelerated by a factor of 1200 at the highest pressure. The results are given in Table 1.

Figure 1 shows that $\log_{10}(k_p/k_1)$ varies smoothly with the pressure, much in the manner of our earlier results to 15,000 atm (David and Hamann 1954). There is no strikingly new behaviour at the higher pressures.

Experimental

(*a*) *Apparatus.*—The pressures were produced by using a hydraulic press to force a piston into a massive steel cylinder containing the pressure fluid. The method was similar to that employed in our earlier measurements to 15000 atm (David and Hamann 1954), but some modifications were needed to reach 30000 atm.

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TABLE 1

EFFECT OF PRESSURE ON THE METHANOLYSIS OF ETHYL CHLORIDE IN PURE METHANOL AT 65 °C

Pressure, p (atm)	Reaction Time (sec)	Percentage Reaction*	First-Order Rate Constant $10^8\,k$ (sec^{-1})	$\frac{k_p}{k_1}$†
1	57600‡	¼‡	4·7	1
3000	90000	3	37	7·9
10000	21600	6	290	62
12500	20700	11	510	109
15000	14400	9	630	134
17500	12600	14	1000	210
20000	10800	16	1560	330
23200	3600	8	2300	490
25100	5400	13	2600	550
27500	1800	6	3400	720
30600	1800	10	5700	1210

* Measured as hydrochloric acid.

† This is the ratio of the rate constant at the pressure p to that at 1 atm.

‡ These two columns list typical results, not all the experimental data.

Firstly, the pressure vessel A (Fig. 2) was given external support in the manner devised by Bridgman (1936). It was made in the form of a cone, of very acute angle, fitting closely into a similar conical hole in a steel supporting ring B. The thrust of the piston C not only produced the internal pressure in A

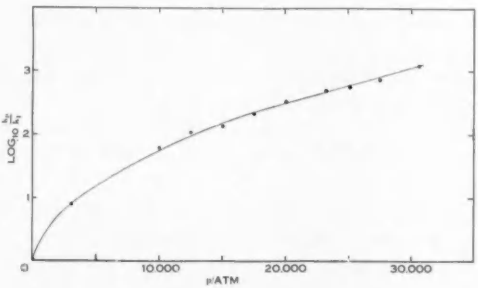

Fig. 1.—The pressure-dependence of the rate of methanolysis of ethyl chloride.

but also forced this vessel into the supporting ring and produced a pressure at its outer surface equal to half the internal pressure.

Secondly, since the limit of the crushing strength of steel is about 25000 atm, it was necessary to make the piston of "Carboloy"* which has a crushing

* "Carboloy" is the trade name for tungsten carbide cemented in cobalt. The grade used was No. 883.

strength of 50000–60000 atm. To ensure that the thrust was applied axially, the piston was mounted in a push-rod *D*, of larger diameter, guided by a cap *E* as used by Poulter (1932). The push-rod was actuated by a 25-ton hydraulic press.

Thirdly, the " unsupported area " seal was modified as suggested by Bridgman (1937*a*), in order to overcome the " pinching-off " effect (Bridgman 1912) in the mushroom stem. Bridgman reported that no difficulty was experienced from failure of the spacing piece *F*, but in our apparatus this proved

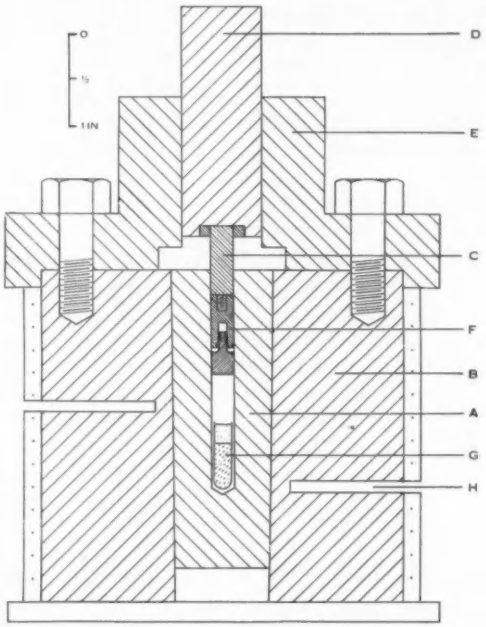

Fig. 2.—The high pressure apparatus.

to be the weakest part. Several types of steel were tried, the most successful being Eagle and Globe " Ultra Capital Plus One " tool steel, heat treated to extreme hardness. Even with this steel, failures occurred above 25000 atm.

The materials used for the other parts of the apparatus were as follows. The pressure vessel *A* and supporting ring *B* were of " Comsteel R4 ", the mushroom of " Comsteel R5 ", and the push-rod of Eagle and Globe " PRN2 " steel. The mushroom was fully hardened and the remaining pieces were quenched from 850 °C and tempered at 200 °C. The tube *G*, containing 0·15 ml of the reaction mixture, was of soda glass sealed by a " Neoprene " plug. It was surrounded by *iso*-propyl alcohol to transmit the pressure from the piston.

The temperature was measured by thermocouples housed in two probe-holes *H*, and was regulated by manual adjustment of the current in a lagged heater wound around the supporting ring. The pressure in *A* was calculated from the oil pressure in the hydraulic press, the relationship between these two pressures being established by some observations, at 23 °C, of the transitions: water (liq.)→ice VI, at 9100 atm (Bridgman 1911) and ice VI→ice VII at 21600 atm (Bridgman 1937*b*).

(*b*) *Procedure.*—The experimental procedure has been described earlier (David and Hamann 1954). The initial concentration of ethyl chloride was about half-molar. The reactions were followed by titrating the hydrochloric acid formed against N/100 barium hydroxide, complete reaction of the 0·15 ml samples, requiring 7·5 ml of the barium hydroxide solution. The measurements at 1 and 3000 atm were made in a much larger apparatus than that shown in Figure 1 and the samples were correspondingly larger.

(*c*) *Results.*—At 1 atm and at 65 °C the reaction proceeded very slowly until, after a week, the concentration of hydrochloric acid reached a steady value equal to about 1 per cent. of the initial concentration of ethyl chloride. The smallness of this yield could mean that the reaction is reversible or that the hydrochloric acid is removed by the possible concurrent reactions:

$$H^+ + Cl^- + CH_3OH \rightarrow CH_3Cl + H_2O,$$
$$H^+ + Cl^- + C_2H_5OCH_3 \rightarrow C_2H_5OH + CH_3Cl.$$

Table 1 shows that the effect of pressure is to increase enormously both the yield of hydrochloric acid and its rate of formation. The values of the first-order rate constants in Table 1 are based on the *initial* rate of formation of hydrochloric acid.

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SOME DERIVATIVES OF 2-BROMOALLYLAMINE*

By J. A. LAMBERTON†

Under the conditions of the modified Gabriel reaction, in which dimethylformamide is used as solvent (Billmann and Cash 1953), 1,2,3-tribromopropane yields *N*-(2-bromoallyl)phthalimide. The constitution of the product is shown conclusively by the formation from it, on ozonolysis, of phthaloyl glycine and formaldehyde.

N-(2-Bromoallyl)phthalimide reacts with hydrazine in methanol (Ing and Manske 1926; Sheehan and Bolhofer 1950) to give 2-bromoallylamine which was converted to its benzoyl and *p*-toluene sulphonyl derivatives. The melting point of the benzoyl derivative (97–98 °C) agrees with that recorded in the literature (Galewsky 1890) but the *p*-toluene sulphonyl compound melts at 69–70 °C and not at 45–46 °C as given by Rudzick (1901).

2-Bromoallylamine was also prepared by the method given in the literature (Paal and Hermann 1889) and converted to its benzoyl and *p*-toluene sulphonyl derivatives. It gave the same benzoyl derivative melting at 97–98 °C but the *p*-toluene sulphonyl derivative was less readily purified when the amine was prepared in this way and had an indefinite m.p. of *c.* 60 °C.

2-Bromoallylamine, prepared by Paal's method, also reacts with phthalic anhydride to give *N*-(2-bromoallyl)phthalimide, identical with the product from the Gabriel reaction. 2,3-Dibromopropylamine reacts similarly to give *N*-(2,3-dibromopropyl)phthalimide, previously prepared by bromination of *N*-allylphthalimide (Neumann 1890).

Experimental

Melting points are uncorrected. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(*a*) *N-(2-Bromoallyl)phthalimide.*—1,2,3-Tribromopropane (8·4 g), phthalimide (13·2 g), anhydrous potassium carbonate (6·2 g), and a trace of potassium iodide were heated in dimethylformamide (30 ml) at 140–145 °C for 2 hr. The mixture was poured into water and the insoluble material filtered. After washing with dilute sodium hydroxide to dissolve some unchanged phthalimide, the product was recrystallized from aqueous ethanol. It formed colourless needles, m.p. 125–126 °C. Yield, 6·5 g (Found: C, 49·7; H, 3·2; N, 4·9; Br, 30·2%. Calc. for $C_{11}H_8O_2NBr$: C, 49·6; H, 3·0; N, 5·3; Br, 30·1%).

Ozonolysis of the phthalimide compound in glacial acetic acid gave phthaloyl glycine (m.p. and mixed m.p. 189–190 °C) and formaldehyde in good yield. Formaldehyde was isolated and identified as its 2,4-dinitrophenylhydrazone and dimedone derivative. Heating with hydrazine in methanol gave phthalhydrazide and 2-bromoallylamine, which was isolated as its hydrochloride.

(*b*) *N-(2-Bromoallyl)benzamide.*—The benzoyl derivative, prepared from 2-bromoallylamine hydrochloride by the Schötten-Baumann method, was obtained as needles from benzene-light

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petroleum, m.p. 97–98 °C (Galewsky reports 97–98 °C) (Found: C, 50·3; H, 4·1; Br, 33·3%. Calc. for $C_{10}H_{10}ONBr$: C, 50·0; H, 4·2; Br, 33·3%).

(*c*) N-(*2-Bromoallyl*) p-*Toluene Sulphonamide.*—Prepared from 2-bromoallylamine hydrochloride by shaking with *p*-toluene sulphonyl chloride and sodium hydroxide solution. Needles from light petroleum, m.p. 69–70 °C (Rudzick gives 45–46 °C) (Found: C, 41·6; H, 4·1; N, 4·6; S, 11·1; Br, 27·3%. Calc. for $C_{10}H_{12}O_2SNBr$: C, 41·4; H, 4·1; N, 4·8; S, 11·0; Br, 27·6%).

2-Bromoallylamine hydrochloride, prepared from 2,3-dibromopropylamine hydrobromide by the method of Paal, gave the same benzoyl derivative, m.p. 97–98 °C, but with *p*-toluene sulphonyl chloride and sodium hydroxide the product was difficult to purify and melted at *c.* 60 °C.

(*d*) N-(*2-Bromoallyl*)*phthalimide.*—When 2-bromoallylamine hydrochloride was heated with phthalic anhydride and sodium acetate in acetic acid, the product was *N*-(2-bromoallyl)phthalimide, m.p. 126–127 °C undepressed by admixture with the product from the Gabriel reaction.

(*e*) N-(*2,3-Dibromopropyl*)*phthalimide.*—2,3-Dibromopropylamine hydrobromide was also heated with phthalic anhydride and sodium acetate in acetic acid solution. It gave *N*-(2,3-dibromopropyl)phthalimide, m.p. 112–114 °C, after crystallization from ethanol (Found: C, 38·3; H, 2·9; Br, 46·0%. Calc. for $C_{11}H_9O_2NBr_2$: C, 38·0; H, 2·6; Br, 46·1%).

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THE ISOLATION OF CHRYSOPHANIC ACID AND PHYSCION FROM *RUMEX HYMENOSEPALUS* TORR.*

By W. E. Hillis†

The tubers of *Rumex hymenosepalus* Torr. (known as canaigre) contain about 25 per cent. of tannin and they have been considered as a commercial source of this material (Rogers and Russell 1944). Recently, investigations were made to ascertain whether they could be grown as an economic crop in certain Australian localities. The roots were analysed for tannin by leaching with acetone : water (1 : 1) at 60 °C by the method of Luvisi and Rogers (1948). In the initial stages of the leaching, the liquor from some samples deposited a bright yellow substance. This was identified as a mixture of chrysophanic acid (1,8-dihydroxy-3-methylanthraquinone) and physcion (6-methoxy-1,8-dihydroxy-3-methylanthraquinone). Chrysophanic acid has been isolated from

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this and other *Rumex* species and " emodin monomethyl ether " (presumably physcion) from several other *Rumex* species (Wehmer 1929). Although emodin (1,6,8-trihydroxy-3-methylanthraquinone) has been reported as the anthraquinone present (U.S. Committee of Agriculture 1878) no trace of it was found.

At least two distinct strains of canaigre are known and they differ in colour, in tannin content, and also in their behaviour in leaching experiments (Rogers 1950–51). In this present work at least two strains were encountered in the 25 samples, one lot of dried tubers were pink-fawn, the other yellow-fawn and the latter deposited most of the anthraquinones. There was a tendency that those tubers which gave the greatest amounts of yellow deposits showed the least vigorous growth and in view of this, it is interesting to note that a 1,4-dihydroxyanthraquinone (quinizarin) retarded the root growth of garden cress (*Lepidium sativum*) whilst certain polyhydroxyanthraquinones containing a 1,2-dihydroxy grouping increased the root growth (Flaig and Otto 1951). As chrysophanic acid and physcion lack a 1,2-dihydroxy grouping they may be associated with the retarded growth of certain canaigre tubers.

Experimental

(*a*) *Isolation of Anthraquinones.*—The tubers of *R. hymenosepalus* grown at Merbein, Vict., were sliced, air-, and finally vacuum-dried at room temperature, and then ground in a Wiley mill to pass a 10 mesh sieve. The samples were extracted in a Soxhlet apparatus with benzene for 3 days to give between 1·2 and 0·3 per cent. extractives. The order of the samples within these limits was about the same as the qualitative assessment of the amount of yellow crystals precipitated during the determination of tannin by the method of Luvisi and Rogers (1948).

The anthraquinones could be recovered from the benzene extracts by sublimation at 125 °C/0·003 mm. The mixture from this source or from Merck " chrysophanic acid " could be partly separated into the acid and physcion by fractional sublimation at 110 °C/0·003 mm. At first a bright orange amorphous substance collected on the condenser and towards the end a yellow substance appeared as a felt of very fine needles. The first fractions were resublimed at 150 °C/1 mm and the orange platelets of chrysophanic acid recrystallized from ethanol. The felts of yellow needles of physcion were resublimed at 110 °C/0·003 mm. Both materials appeared homogeneous by paper chromatographic examination.

The components were obtained in a pure form by applying a streak of an acetone solution of the canaigre root extract to a Whatman No. 3 MM paper (22 by 18 in.). The chromatogram was developed at 22 °C by capillary ascent for 18 hr with a solvent prepared by saturating methanol with *n*-hexane at 10 °C (this was more reliable than the solvent of Shibata, Takito, and Tanaka 1950). The paper was examined under ultraviolet light immediately it was removed from the tank and the orange (R_F 0·71) and the yellow band (R_F 0·56) outlined and cut out. The components were eluted with cold acetone from the strips obtained from 30 papers, filtered, and evaporated under vacuum at room temperatures, and both sublimed at 110 °C under high vacuum and crystallized from ethanol. The acetate of the material with R_F 0·71 did not depress the melting point of authentic chrysophanic acid diacetate, and the material with R_F 0·56 did not depress the melting point of physcion.

(*b*) *Identification of Chrysophanic Acid.*—The sample obtained by sublimation dissolved in conc. H_2SO_4 to give a purple-red colour, and in 2N NaOH to give a red solution, it slowly dissolved in strong NH_3 solution to give a blue-red colour. It was insoluble in cold 5 per cent. Na_2CO_3 and an alcoholic solution became more strongly yellow with ferric chloride, m.p. and mixed m.p. with authentic chrysophanic acid was 192–194 °C. A 0·00004M methanolic solution exhibited maxima at 427, and 283 mμ (log ε 4·05, and 4·03) when measured in a Unicam Model SP 500 Quartz Spectrophotometer.

Chrysophanic acid (50 mg) was acetylated with acetic anhydride (3 ml) and perchloric acid (1 drop ; 70%) overnight. The product obtained by pouring the mixture into water was recrystallized from ethanol, m.p. 200–203 °C, yield 55 mg. After sublimation (150–160 °C/10^{-3} mm) and several recrystallizations from ethanol, the pale yellow plates of the diacetate had m.p. of 207–208 °C, mixed m.p. unchanged (Found : C, 67·7 ; H, 4·2%. Calc. for $C_{19}H_{14}O_6$: C, 67·5 ; H, 4·2%).

(c) *Identification of Physcion.*—The felt of yellow needles obtained at the end of the sublimation gave colour reactions identical with those given by chrysophanic acid when examined simultaneously. It had m.p. and mixed m.p. 205–206 °C (Found : C, 67·8 ; H, 4·4%. Calc. for $C_{16}H_{12}O_5$: C, 67·6 ; H, 4·2%). A 0·00004M methanolic solution exhibited maxima at 427 and 280 mμ (log ε 4·12 and 4·19).

The substance (3 mg) was acetylated with acetic anhydride (1 ml) and perchloric acid (1 drop ; 70%) for 3 hr. The product obtained by pouring the mixture into water was recrystallized four times from methanol, m.p. 187·5–188 °C (lit. for physcion diacetate, m.p. 186–187 °C (Ashley, Raistrick, and Richards 1939 ; Seshadri and Subramaman 1949)).

The author is grateful for the assistance of Miss Ann Carle with the chromatographical work. Professor A. J. Birch kindly supplied the Merck " Chrysophanic acid " and Dr. H. Duewell the authentic specimens of chrysophanic acid, its acetate, and physcion.

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Corrigenda

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Page 97, line 4 from bottom : *For* $C_{12}H_{12}O_4$ *read* $C_{12}H_{14}O_4$.
Page 99, line 23 : *For* 14870 *read* 1·4870.
Page 116 : The pyran ring in (III) should be a furan ring as in (IV) and (V).
Page 125, line 21 : *For* $C_{26}H_{30}O_7N_4$ *read* $C_{21}H_{20}O_7N_4$.
Page 126 : Dihydrodeoxygeijerin as shown in (III) contains a double bond in the 3,4-position which should be replaced by a single bond.
Page 126, line 4 from bottom : *For* 26 *read* 260.
Page 126, bottom line : *For* $C_{26}H_{30}O_7H_4$ *read* $C_{21}H_{20}O_7N_4$.
Page 127, line 4 : *For* $C_{15}H_{17}O_4$ *read* $C_{15}H_{18}O_4$.
Page 138, line 11 from bottom : *For* $C_{15}H_{22}ON_2.\frac{1}{2}H_2O$ *read* $C_{15}H_{23}ON_2.HClO_4.\frac{1}{2}H_2O$.